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QM/MM METHODS FOR CRYSTALLINE DEFECTS. PART 2: CONSISTENT ENERGY AND FORCE-MIXING*

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Abstract. We develop and analyze QM/MM (quantum/classic) hybrid methods for crystalline defects within the context of the tight-binding model. QM/MM methods employ accurate quantum mechanics (QM) models only in regions of interest (defects) and switch to computationally cheaper interatomic potential molecular mechanics (MM) models to describe the crystalline bulk. We propose new energy-based and force-based QM/MM methods, building on two principles: (i) locality of the QM model; and (ii) constructing the MM model as an explicit and controllable approximation of the QM model. This approach enables us to rigorously establish convergence rates in terms of the size of the QM region.

Key words. QM/MM coupling, energy-based, force-based, convergence rates

AMS subject classifications. 65N12, 65N25, 70C20, 81V45

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1. Introduction.

Algorithms for concurrently coupling quantum mechanics and classical molecular mechanics (QM/MM) are widely used to perform simulations of large systems in materials science and biochemistry [3, 8, 13, 17, 22, 32, 33]. A quantum mechanics (QM) model is necessary for accurate treatments of bond breaking/formation, charge transfer, electron excitation, and so on. However, the applications of QM is limited to systems with hundreds of atoms due to the significant computational cost. By contrast, molecular mechanics (MM) methods based on empirical interatomic potentials are able to treat millions of atoms or more but have reduced accuracy (more precisely, they are not transferable). QM/MM coupling methods promise (near-)QM accuracy at (near-)MM computational cost for large-scale atomistic simulations in materials science.

In QM/MM simulations the computational domain is partitioned into two regions. The region of primary interest, described by a QM model, is embedded in an environment (e.g., bulk crystal) which is described by an MM model. The coupling between these two regions is the key challenge in the construction of accurate and efficient QM/MM methods.

A natural question is the accuracy of QM/MM models as a function of QM region size. The number of atoms in the QM region is a discretization parameter, and the observables of interest should converge to the desired accuracy with respect to this parameter. Despite the growing number of QM/MM methods and their applications, few publications have included quantitative tests of the accuracy of the method and its convergence with respect to possible parameters. To the best of our knowledge, there is no theoretical analysis of QM/MM methods in the literature.

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The purpose of this paper is to initiate a numerical analysis of QM/MM methods. We develop two new QM/MM methods for crystalline defect simulations for which we can prove rigorous a priori error estimates. We use the tight-binding (TB) model (a minimalist QM method) as the QM model and, for the MM region, *construct* an interatomic potential (or forces) through an explicit approximation of the TB model, which is reminiscent of the force-matching technique [11]. This approach enables us to establish explicit convergence rates in terms of the size of the QM region.

Our analysis is based on two key preliminaries: the "strong locality" of the (finite temperature) TB model [6] and the decay estimates of equilibria in lattices with defects [5, 9].

Outline. In section 2, we review the existing QM/MM methodology for material systems. In section 3, we review the TB model for crystalline defects which we use as the QM model. In sections 4 and 5, we construct QM/MM coupling schemes with rigorous error estimates based, respectively, on energy-mixing and force-mixing principles. Finally, we summarize our findings and make some concluding remarks concerning practical aspects which we will pursue in forthcoming work.

Notation. We will use the symbol $\langle \cdot, \cdot \rangle$ to denote an abstract duality pairing between a Banach space and its dual. The symbol $|\cdot|$ normally denotes the Euclidean or Frobenius norm, while $\|\cdot\|$ denotes an operator norm. For the sake of brevity, we will denote $A \backslash \{a\}$ by $A \backslash a$ and $\{b - a \mid b \in A\}$ by $A - a$.

For a differentiable function f, ∇f denotes the Jacobi matrix. For $E \in C^2(X)$, the first and second variations are denoted by $\langle \delta E(u), v \rangle$ and $\langle \delta^2 E(u) w, v \rangle$ for $u, v, w \in X$. For higher variations, we will use the notation $\delta^k E(u_0)[u_1, \ldots, u_k]$, and $\delta^k E(u_0)[u^{\otimes k}]$ for abbreviation when $u_1 = \cdots = u_k = u$.

For $j \in \mathbb{N}$, $\boldsymbol{g} \in (\mathbb{R}^d)^A$, and $V \in C^j\big((\mathbb{R}^d)^A\big)$, we define the notation

$$V_{,\boldsymbol{\rho}}(\boldsymbol{g}) := \frac{\partial^j V(\boldsymbol{g})}{\partial \boldsymbol{g}_{\rho_1}, \ldots, \partial \boldsymbol{g}_{\rho_j}} \quad \text{for} \quad \boldsymbol{\rho} = (\rho_1, \ldots, \rho_j) \in A^j.$$

The symbol C denotes the generic positive constant that may change from one line of an estimate to the next. When estimating rates of decay or convergence, C will always remain independent of system size, lattice position, or test functions. The dependencies of C will normally be clear from the context or stated explicitly.

2. QM/MM coupling methods.

The many different variants to couple QM and MM models can be broadly divided into two categories: energy-mixing and force-mixing. Energy-mixing methods define an energy functional that involves mixture of QM and MM energies, and the solution is obtained by minimizing the energy functional. By contrast, force-mixing methods define a system of force balance equations, where the forces involve contributions from QM and MM models and are nonconservative (i.e., they are not compatible with any energy functional). In the present section we review both classes of QM/MM schemes for materials systems.

2.1. Energy-mixing.

The system under consideration is partitioned into QM and MM regions (see Figure 1 for two examples). Let y^{QM} and y^{MM} denote the respective atomic configurations in these two regions. Depending on the construction of the hybrid total energy E, energy-based methods can mainly be divided into two categories.

(1) In the *subtractive approach*, e.g., the *ONIOM* method [18, 22, 29] and its

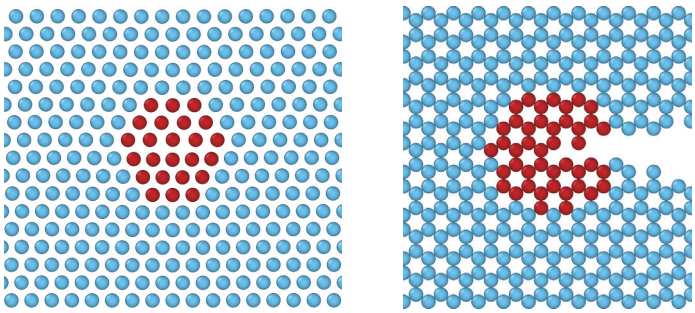

FIG. 1. *Partition of QM and MM regions for an edge dislocation in a 2D triangular lattice and crack in the 2D hexagonal lattice (cartoons). The dislocation core and a small neighborhood belong to the QM region (red/dark), while the bulk crystal behaves purely elastically and can therefore be well described by an empirical interatomic potential (blue/light).*

derivatives,

$$E(y^{\mathrm{QM}\cup\mathrm{MM}}) = E^{\mathrm{MM}}(y^{\mathrm{QM}\cup\mathrm{MM}}) + E^{\mathrm{QM}}(y^{\mathrm{QM}}) - E^{\mathrm{MM}}(y^{\mathrm{QM}}); \tag{1}$$

that is, an MM energy for the entire system is corrected by the difference between the QM and MM energies of the QM region.

(2) In the *additive approach*, e.g., *ChemShell* [20], *DL-FIND* [16], *MAAD* [4], and *QUASI* [27], the QM energy of the QM region and MM energy of the MM region are connected via an interaction energy which may depend on an interface that involves parts of both regions,

$$E(y^{\mathrm{QM}\cup\mathrm{MM}}) = E^{\mathrm{QM}}(y^{\mathrm{QM}}) + E^{\mathrm{MM}}(y^{\mathrm{MM}}) + E^{\mathrm{interaction}}(y^{\mathrm{QM}}, y^{\mathrm{MM}}). \tag{2}$$

The advantage of energy-based methods is that they are naturally energy conserving. Unfortunately, the spurious interface effects acting between the QM and MM regions can be significant. To alleviate such effects, the QM and MM regions are either "passivated" [27, 28] or "buffered" [21, 22]. In the first approach, the energies $E^{\mathrm{QM}}(y^{\mathrm{QM}})$ in (1) and (2) are the energies of the passivated cluster of the QM region, in which a number of additional atoms that have no counterparts in the real system (for example, hydrogen atoms) are added to the QM region to terminate the broken bonds. The second approach handles the boundary by defining buffer layers surrounding the QM and MM regions, so that each atom can see a full complement of surrounding atoms.

The second approach seems to be preferred in solid state systems since the elimination of the boundary effects for passivated atoms will not be perfect and may indeed be severe [7]. The simplest example is for a perfect bulk system, where the true force on all atoms is zero. However, the passivated cluster force computed with QM and MM will in general be nonzero on the passivation atoms and nearby atoms [3]. This is reminiscent of the ghost forces which are a well-understood concept in atomistic/continuum multiscale methods [19].

2.1.1. An idealized hybrid model. In addition to the widely used *subtractive* and *additive* approaches, there is a third type of energy-based formulation, called the *local energy approach*, which mixes local energies computed by QM and MM methods in their respective regions:

$$E(y^{\mathrm{QM}\cup\mathrm{MM}}) = \sum_{\ell\in\mathrm{QM}} E_\ell^{\mathrm{QM}}(y^{\mathrm{QM}\cup\mathrm{MM}}) + \sum_{\ell\in\mathrm{MM}} E_\ell^{\mathrm{MM}}(y^{\mathrm{QM}\cup\mathrm{MM}}) \tag{3}$$

with E_ℓ denoting the local energy associated to the ℓth atomic site. Even though the expression (3) seems intuitive, this variant is not commonly used in QM/MM coupling schemes. Indeed, we are only aware of a brief reference to this approach in [3]. The reason is that it was unclear how to decompose E into local contributions $E_\ell^{\rm QM}$ that match with a classical interatomic potential site energy $E_\ell^{\rm MM}$.

In the previous work of this series [6], we studied the TB site energy introduced in [10, 12] and justified its "strong locality" rigorously. This is important and useful in QM/MM coupling schemes based on (3) since (1) when using classical potentials the total energy is almost always written as a sum over atoms $E = \sum_\ell E_\ell$; therefore, we are able to establish the bridge between the electronic and classical worlds; (2) rather than using "black-box" MM potentials, we can construct MM site energies based on the approximations of QM site energies for good coupling of the different models.

It is pointed out in [3] that matching the force-constant/dynamic matrix (i.e., the first order derivatives of the force or the second order derivatives of the energy with respect to atomic positions) would guarantee a perfect match between the MM and QM forces for arbitrary infinitesimal displacements from equilibrium. In case of an energy-based method, only such a strict matching criterion can guarantee that spurious forces are eliminated for near-equilibrium configurations. The errors resulting from mismatching the force-constant/dynamic matrix are analogous to so-called *ghost forces* in atomistic/continuum hybrid schemes.

Based on these observations, we construct an idealized MM site energy by taking the second order expansion of $E_\ell^{\rm QM}$:

$$E_\ell^{\rm lin}(y) := E_\ell^{\rm QM}(y_0) + \big\langle \delta E_\ell^{\rm QM}(y_0), y - y_0 \big\rangle + \frac{1}{2}\big\langle \delta^2 E_\ell^{\rm QM}(y_0)(y - y_0), y - y_0 \big\rangle, \tag{4}$$

where $y = y^{\rm QM\cup MM}$ and y_0 is a predicted (near-)equilibrium configuration, typically the far-field crystalline environment or an explicit linearized elasticity solution. The QM/MM total energy (3) is then given by

$$E(y) = \sum_{\ell\in{\rm QM}} E_\ell^{\rm QM}(y) + \sum_{\ell\in{\rm MM}} E_\ell^{\rm lin}(y). \tag{5}$$

Equation (5) gives rise to a simple QM/MM coupling scheme, in which the MM potential is constructed such that it matches the QM model. Matching of the MM and QM models for higher order information can also become important, e.g., for slowly decaying elastic fields (dislocations, cracks) or due to increased temperature which may cause fluctuations to displacements beyond the quadratic regime [3]. We will therefore discuss arbitrary order expansions in this paper.

2.2. Force-mixing. With the partition of QM and MM regions, the force-based methods combine QM forces for atoms in the QM region with MM forces in the MM region. The simplest variant, *brutal force-mixing* [7], is defined by

$$F_\ell(y^{\rm QM\cup MM}) = \begin{cases} F_\ell^{\rm QM}(y^{\rm QM\cup MM}) & \text{if } \ell \in {\rm QM}, \\ F_\ell^{\rm MM}(y^{\rm QM\cup MM}) & \text{if } \ell \in {\rm MM}. \end{cases} \tag{6}$$

Typically, the QM and MM forces are computed by carving a cluster buffered by a layer of atoms defined by a distance cutoff, and the forces on all the buffer atoms are discarded [7]. In other variants, a transition region is introduced where forces are smoothly blended [7]. Examples of force-mixing QM/MM methods are *DCET* [1, 2] and *LOTF* [8, 31].

The main advantage of force-mixing is that there are no spurious interface forces as in energy-mixing schemes. However, this comes at the cost of a nonconservative force field. Moreover, if the QM and MM forces are directly used (without modification) for molecular dynamics simulations, then the dynamics will not conserve momentum [3].

2.2.1. An idealized model. Similar to the discussions for energy-mixing methods, we will construct MM forces by an expansion of QM forces so that the force-constant/dynamic matrix can be matched, e.g., with a first order expansion,

$$F_\ell^{\rm MM}(y) := F_\ell^{\rm lin}(y) := F_\ell^{\rm QM}(y_0) + \big\langle \delta F_\ell^{\rm QM}(y_0), y - y_0 \big\rangle, \tag{7}$$

where $y = y^{\rm QM\cup MM}$ and y_0 is a suitable predictor of the equilibrium configuration. For the same reasons as in the energy-mixing approach, we will also consider higher order expansions of the forces.

Remark 2.1. Our construction of the MM site energies and of the MM forces is reminiscent of the classical idea of *force matching*. This is usually applied to the construction of interatomic potentials [11] and has more recently been applied in a coupling context, e.g., in [8, 30]. A key difference in our present work, in the energy-based variant, is that we match the site energies rather than the total energies (and forces).

3. Tight-binding model for crystalline defects. A finite or countable index-set $\Lambda \subset \mathbb{R}^m$ is called a *reference configuration*. A deformed configuration is described by a map $y : \Lambda \to \mathbb{R}^d$ with $m, d \in \{2, 3\}$ denoting the space dimensions. (Allowing $m \neq d$ allows us to define two-dimensional (2D) models of straight dislocations.)

We say that the map y is a *proper configuration* if the atoms do not accumulate:

$$\mathbf{L}. \quad \exists\, \mathfrak{m} > 0 \ \text{ such that } \ |y(\ell) - y(k)| \geq \mathfrak{m}|\ell - k| \quad \forall\, \ell, k \in \Lambda.$$

Throughout, we let $\mathcal{V}_\mathfrak{m} \subset \big(\mathbb{R}^d\big)^\Lambda$ denote the subset of all $y \in (\mathbb{R}^d)^\Lambda$ satisfying $\mathbf{L}$. If we need to emphasize the domain Λ, then we will write $\mathcal{V}_\mathfrak{m}(\Lambda)$.

3.1. The tight-binding model and its site energy. The TB model is a minimalist QM-type model, which enables the investigation and prediction of properties of molecules and materials. For simplicity of presentation, we consider a "two-center" TB model [14, 26] with a single orbital per atom and the identity overlap matrix. All results can be extended directly to general non–self-consistent TB models, as described in [6].

For a finite system with reference configuration Ω, $\#\Omega = N$, the two-center TB model is formulated in terms of a discrete Hamiltonian, with the matrix elements

$$\Big(\mathcal{H}(y)\Big)_{\ell k} = \begin{cases} h_{\rm ons}\Big(\sum_{j\neq\ell} \varrho\big(|y(\ell) - y(j)|\big)\Big) & \text{if } \ell = k, \\ h_{\rm hop}\big(|y(\ell) - y(k)|\big) & \text{if } \ell \neq k, \end{cases} \tag{8}$$

where $R_{\rm c}$ is a cutoff radius, $h_{\rm ons} \in C^{\mathfrak{n}}([0,\infty))$ is the on-site term, with $\varrho \in C^{\mathfrak{n}}([0,\infty))$, $\varrho = 0$ in $[R_{\rm c}, \infty)$, and $h_{\rm hop} \in C^{\mathfrak{n}}([0,\infty))$ is the hopping term with $h_{\rm hop}(r) = 0\ \forall r \in [R_{\rm c}, \infty)$.

Our results can be generalized to the more general TB model presented in [6], but for the sake of simplicity of notation, we restrict ourselves to (8), which still includes most non–self-consistent TB models in the literature.

Note that $h_{\rm ons}$ and $h_{\rm hop}$ are independent of ℓ and k, which indicates that all atoms of the system belong to the same species. We observe that the formulation (8) satisfies all the assumptions on Hamiltonian matrix elements in [6, Assumptions **H.tb, H.loc, H.sym, H.emb**].

With the above TB Hamiltonian $\mathcal{H}$, we can obtain the band energy of the system

$$E^{\Omega}(y) = \sum_{s=1}^{N} f(\varepsilon_s)\varepsilon_s, \tag{9}$$

where $(\varepsilon_s)_{s=1}^N$ are the eigenvalues of $\mathcal{H}(y)$, with associated eigenvectors ψ_s,

$$\mathcal{H}(y)\psi_s = \varepsilon_s\psi_s, \quad s = 1, 2, \ldots, N, \tag{10}$$

f is the Fermi–Dirac function,

$$f(\varepsilon) = \left(1 + e^{(\varepsilon-\mu)/(k_{\rm B}T)}\right)^{-1}, \tag{11}$$

μ is a fixed chemical potential, $k_{\rm B}$ is Boltzmann's constant, and $T > 0$ is the temperature of the system. We do not consider the pairwise repulsive potential, which can be treated purely classically [6].

Following [12], we can distribute the energy to each atomic site

$$E^{\Omega}(y) = \sum_{\ell\in\Omega} E_\ell^{\Omega}(y) \qquad \text{with} \qquad E_\ell^{\Omega}(y) := \sum_s f(\varepsilon_s)\varepsilon_s \left|[\psi_s]_\ell\right|^2. \tag{12}$$

The following theorem [6, Theorem 3.1(i)] states the existence of the limit as $\Omega \uparrow \Lambda$, $\Omega \subset \Lambda$, for some countable reference domain Λ. For an infinite body, Λ, we will denote this limit site energy by E_ℓ. We will continue to denote the site energies of subsystems $\Omega \subset \Lambda$ by E_ℓ^{Ω}. When Λ is an infinite reference configuration and $A \subset \mathbb{R}^m$, then we will also use the shorthand $E_\ell^A := E_\ell^{A\cap\Lambda}$.

THEOREM 3.1. *Suppose Λ is countable, $y \in \mathcal{V}_{\mathfrak{m}}(\Lambda)$ is a deformation, and $\Omega \subset \Lambda$ is a finite subset. Then the following hold.*

(i) (Regularity and locality of the site energy) *$E_\ell^{\Omega}(y)$ possesses jth order partial derivatives with $1 \le j \le \mathfrak{n} - 1$, and there exist positive constants C_j and η_j such that*

$$\left|\frac{\partial^j E_\ell^{\Omega}(y)}{\partial[y(m_1)]_{i_1}\cdots\partial[y(m_j)]_{i_j}}\right| \le C_j e^{-\eta_j \sum_{l=1}^{j} |y(\ell)-y(m_l)|} \tag{13}$$

with $m_k \in \Omega$ and $1 \le i_k \le d$ for any $1 \le k \le j$.

(ii) (Isometry invariance) *$E_\ell^{\Omega}(y) = E_\ell^{\Omega}(g(y))$ if $g : \mathbb{R}^d \to \mathbb{R}^d$ is an isometry.*

(iii) (Permutation invariance) *$E_\ell^{\Omega}(y) = E_{\mathcal{G}^{-1}(\ell)}^{\mathcal{G}^{-1}(\Omega)}(y\circ\mathcal{G})$ for a permutation $\mathcal{G} : \Lambda \to \Lambda$.*

(iv) (Thermodynamic limit) *$E_\ell(y) := \lim_{R\to\infty} E_\ell^{B_R(\ell)}(y)$ exists and satisfies* (i), (ii), *and* (iii) *with $\Omega = \Lambda$.*

For a finite subset $\Omega \subset \Lambda$, we define the (negative) force

$$F^{\Omega}(y) := \nabla E^{\Omega}(y); \text{ in component notation, } \left[F_\ell^{\Omega}(y)\right]_i = \frac{\partial E^{\Omega}(y)}{\partial[y(\ell)]_i} \quad 1 \le i \le d. \tag{14}$$

Using (12), we have

$$\big[F_\ell^\Omega(y)\big]_i = \sum_{k\in\Omega} \frac{\partial E_k^\Omega(y)}{\partial [y(\ell)]_i}, \tag{15}$$

which, together with Theorem 3.1, yields the thermodynamic limit of the force, as well as its regularity, locality, and isometry/permutation invariance.

THEOREM 3.2. *Suppose the assumptions of Theorem* 3.1 *are satisfied. Then the following hold.*

(i) (Regularity and locality of the force) $F_\ell^\Omega(y)$ *possesses* j*th order partial derivatives with* $1 \le j \le \mathfrak{n}-2$*, and there exist positive constants* C_j *and* η_j *such that*

$$\left| \frac{\partial^j F_\ell^\Omega(y)}{\partial [y(m_1)]_{i_1} \cdots \partial [y(m_j)]_{i_j}} \right| \le C_j e^{-\eta_j \sum_{l=1}^j |y(\ell)-y(m_l)|} \tag{16}$$

with $m_k \in \Omega$ *and* $1 \le i_k \le d$ *for any* $1 \le k \le j$.

(ii) (Isometry invariance) $F_\ell^\Omega\big(Qy+c\big) = Q^{\mathrm{T}} F_\ell^\Omega(y)$ *for all* $Q \in \mathrm{SO}(d), c \in \mathbb{R}^d$.

(iii) (Permutation invariance) $F_\ell^\Omega(y) = F_{\mathcal{G}^{-1}(\ell)}^{\mathcal{G}^{-1}(\Omega)}(y \circ \mathcal{G})$ *for a permutation* $\mathcal{G} : \Lambda \to \Lambda$.

(iv) (Thermodynamic limit) $F_\ell(y) := \lim_{R\to\infty} F_\ell^{B_R(\ell)}(y)$ *exists and satisfies* (i), (ii), *and* (iii) *with* $\Omega = \Lambda$.

3.2. Crystalline defects.

3.2.1. Energy space. Let $\Lambda \subset \mathbb{R}^m$ be an infinite reference configuration satisfying $\Lambda \setminus B_{R_{\mathrm{DEF}}} = (A\mathbb{Z}^m) \setminus B_{R_{\mathrm{DEF}}}$ where $R_{\mathrm{DEF}} \ge 0$, $A \in \mathrm{SL}(m)$, and $\Lambda \cap B_{R_{\mathrm{DEF}}}$ is finite. For analytical purposes, we assume that there is a regular partition $\mathcal{T}_\Lambda$ of $\mathbb{R}^m$ into triangles if $m = 2$ and into tetrahedra if $m = 3$, whose nodes are the reference sites Λ (see Appendix A for interpolations of lattice functions on this background mesh).

We can decompose the deformation

$$y(\ell) = y_0(\ell) + u(\ell) = P\ell + u_0(\ell) + u(\ell) \quad \forall\, \ell \in \Lambda, \tag{17}$$

where $u_0 : \Lambda \to \mathbb{R}^d$ is a predictor prescribing the far-field boundary condition, $u : \Lambda \to \mathbb{R}^d$ is a corrector, and $P \in \mathbb{R}^{d\times m}$ denotes a macroscopically applied deformation.

If $\ell \in \Lambda$ and $\ell+\rho \in \Lambda$, then we define the finite difference $D_\rho u(\ell) := u(\ell+\rho)-u(\ell)$. If $\mathcal{R} \subset \Lambda - \ell$, then we define $D_\mathcal{R} u(\ell) := (D_\rho u(\ell))_{\rho\in\mathcal{R}}$, and $Du(\ell) := D_{\Lambda-\ell} u(\ell)$. For a stencil $Du(\ell)$ and $\gamma > 0$ we define the (semi)norms

$$\big|Du(\ell)\big|_\gamma := \bigg(\sum_{\rho\in\Lambda-\ell} e^{-2\gamma|\rho|} \big|D_\rho u(\ell)\big|^2 \bigg)^{1/2} \quad \text{and} \quad \|Du\|_{\ell^2_\gamma} := \bigg(\sum_{\ell\in\Lambda} |Du(\ell)|_\gamma^2 \bigg)^{1/2}.$$

An immediate consequence of (88) is that all (semi)norms $\|\cdot\|_{\ell^2_\gamma}, \gamma > 0$, are equivalent.

We can now define the natural function space of finite-energy displacements,

$$\dot{\mathscr{W}}^{1,2} := \big\{ u : \Lambda \to \mathbb{R}^d, \|Du\|_{\ell^2_\gamma} < \infty \big\}.$$

3.2.2. Site energy. Let E_ℓ denote the site energies we defined in Theorem 3.1(iv). Because they are translation invariant, we can define $V_\ell : (\mathbb{R}^m)^{\Lambda-\ell} \to \mathbb{R}$ by

$$V_\ell(Du) := E_\ell(Px_0 + u) \qquad \text{with} \quad x_0 : \Lambda \to \mathbb{R}^d \ \text{ and } \ x_0(\ell) = \ell \ \ \forall\, \ell \in \Lambda. \tag{18}$$

For a displacement u satisfying $y_0 + u \in \mathcal{V}_{\mathfrak{m}}(\Lambda)$, we can define (formally, for now) the energy-difference functional

$$\mathcal{E}(u) := \sum_{\ell\in\Lambda} \Big(E_\ell(y_0+u) - E_\ell(y_0)\Big) = \sum_{\ell\in\Lambda} \Big(V_\ell(Du_0(\ell) + Du(\ell)) - V_\ell(Du_0(\ell))\Big). \tag{19}$$

For both point defects and dislocations, we can construct predictors y_0 (see sections 3.2.3 and 3.2.4) such that $\delta\mathcal{E}(0) \in (\dot{\mathscr{W}}^{1,2})^*$. We prove in [5] (see also [9, Lemma 2.1]) that, under this condition, $\mathcal{E}$ is well defined on the space Adm_0 and in fact $\mathcal{E} \in C^{\mathrm{n}-1}(\mathrm{Adm}_0)$, where

$$\mathrm{Adm}_{\mathfrak{m}} := \big\{u \in \dot{\mathscr{W}}^{1,2},\ |y_0(\ell) + u(\ell) - y_0(m) - u(m)| > \mathfrak{m}|\ell - m| \quad \forall\, \ell, m \in \Lambda\big\}.$$

Due to the decay imposed by the condition $u \in \dot{\mathscr{W}}^{1,2}$, any displacement $u \in \mathrm{Adm}_0$ belongs to $\mathrm{Adm}_{\mathfrak{m}}$ with some constant $\mathfrak{m} > 0$. In sections 3.2.3 and 3.2.4 we show how the crucial condition $\delta\mathcal{E}(0) \in (\dot{\mathscr{W}}^{1,2})^*$ is obtained for, respectively, point defects and dislocations. In section 3.2.5 we then present a unified description for which we then rigorously state the properties of $\mathcal{E}$ and the associated variational problem.

3.2.3. Point defects. We make the following standing assumptions for point defects:

P. $m = d \in \{2, 3\}$; $\exists\, R_{\mathrm{DEF}} > 0, A \in \mathrm{SL}(m)$ such that $\Lambda \backslash B_{R_{\mathrm{DEF}}} = (A\mathbb{Z}^m)\backslash B_{R_{\mathrm{DEF}}}$ and $\Lambda \cap B_{R_{\mathrm{DEF}}}$ is finite; $P = \mathbf{Id}$; $u_0 = 0$; $y_0(\ell) = \ell$.

3.2.4. Dislocations. The following derivation is not essential to our analysis of QM/MM schemes and can indeed be found in [9]; however, for the sake of completeness, we still present enough detail to justify the unified formulation in section 3.2.5.

We consider a model for straight dislocation lines obtained by projecting a three-dimensional (3D) crystal. For a 3D lattice $B\mathbb{Z}^3$ with dislocation direction parallel to e_3 and Burgers vector $\mathsf{b} = (b_1, 0, b_3)$, we consider displacements $W : B\mathbb{Z}^3 \to \mathbb{R}^3$ that are periodic in the direction of the dislocation direction e_3. Thus, we choose a projected reference lattice $\Lambda := A\mathbb{Z}^2 = \{(\ell_1, \ell_2) \mid \ell = (\ell_1, \ell_2, \ell_3) \in B\mathbb{Z}^3\}$, which is again a Bravais lattice. This projection gives rise to a projected 2D site energy with the additional invariance

$$E_\ell(y) = E_\ell(y + ze_3) \quad \forall z : \Lambda \to \mathsf{b}_3\mathbb{Z}. \tag{20}$$

Let $\hat{x} \in \mathbb{R}^2$ be the position of the dislocation core and $\Gamma := \{x \in \mathbb{R}^2 \mid x_2 = \hat{x}_2,\ x_1 \geq \hat{x}_1\}$ be the "branch cut," with $\hat{x}$ chosen such that $\Gamma \cap \Lambda = \emptyset$. Following [9], we define the far-field predictor u_0 by

$$u_0(x) := u^{\mathrm{lin}}(\xi^{-1}(x)), \tag{21}$$

where $u^{\mathrm{lin}} \in C^\infty(\mathbb{R}^2 \setminus \Gamma; \mathbb{R}^d)$ is the continuum linear elasticity solution (see [9] for the details) and

$$\xi(x) = x - \mathsf{b}_{12}\frac{1}{2\pi}\eta\left(\frac{|x - \hat{x}|}{\hat{r}}\right)\arg(x - \hat{x}), \tag{22}$$

with $\arg(x)$ denoting the angle in $(0, 2\pi)$ between x and $\mathsf{b}_{12} = (\mathsf{b}_1, \mathsf{b}_2) = (\mathsf{b}_1, 0)$, and $\eta \in C^\infty(\mathbb{R})$ with $\eta = 0$ in $(-\infty, 0]$, $\eta = 1$ in $[1, \infty)$ removes the singularity.

The predictor $y_0 = Px + u_0$ is constructed in such a way that y_0 jumps across Γ, which encodes the presence of the dislocation. But there is an ambiguity in this

definition in that we could have equally placed the jump into the left half-plane $\{x_1 \le \hat{x}_1\}$. The role of ξ in the definition of u_0 is that applying a plastic slip across the plane $\{x_2 = \hat{x}_2\}$ via the definition

$$y^S(x) := \begin{cases} y(\ell), & \ell_2 > \hat{x}_2, \\ y(\ell - \mathsf{b}_{12}) - \mathsf{b}_3 e_3, & \ell_2 < \hat{x}_2, \end{cases}$$

achieves exactly this transfer: it leaves the (3D) configuration invariant while generating a new predictor $y_0^S \in C^\infty(\Omega_\Gamma)$ where $\Omega_\Gamma = \{x_1 > \hat{x}_1 + \hat{r} + \mathsf{b}_1\}$. Since the map $y \mapsto y^S$ represents a relabeling of the atom indices and an integer shift in the out-of-plane direction, we can apply (20) and Theorem 3.1(iii) to obtain

$$E_\ell(y) = E_{S^*\ell}(y^S), \tag{23}$$

where S is the ℓ^2-orthogonal operator with inverse $S^* = S^{-1}$ defined by

$$Su(\ell) := \begin{cases} u(\ell), & \ell_2 > \hat{x}_2, \\ u(\ell - \mathsf{b}_{12}), & \ell_2 < \hat{x}_2, \end{cases} \quad \text{and} \quad S^*u(\ell) := \begin{cases} u(\ell), & \ell_2 > \hat{x}_2, \\ u(\ell + \mathsf{b}_{12}), & \ell_2 < \hat{x}_2. \end{cases}$$

We can translate (23) into a statement about u_0 and V_ℓ. Let $S_0 w(x) = w(x), x_2 > \hat{x}_2$, and $S_0 w(x) = w(x - \mathsf{b}_{12}) - \mathsf{b}, x_2 < \hat{x}_2$; then we obtain that $y_0^S = Px + S_0 u_0$ and $S_0 u_0 \in C^\infty(\Omega_\Gamma)$ and $S_0(u_0 + u) = S_0 u_0 + Su$. The permutation invariance (23) can now be rewritten as an invariance of V_ℓ under the slip S_0:

$$V\big(D(u_0 + u)(\ell)\big) = V\big(e(\ell) + \widetilde{D}u(\ell)\big) \quad \forall u \in \mathrm{Adm}_0,\ \ell \in \Lambda, \tag{24}$$

where

$$e(\ell) := (e_\rho(\ell))_{\rho \in \Lambda - \ell} \quad \text{with} \quad e_\rho(\ell) := \begin{cases} S^* D_\rho S_0 u_0(\ell), & \ell \in \Omega_\Gamma, \\ D_\rho u_0(\ell), & \text{otherwise}, \end{cases} \tag{25}$$

and

$$\widetilde{D}u(\ell) := (\widetilde{D}_\rho u(\ell))_{\rho \in \Lambda - \ell} \quad \text{with} \quad \widetilde{D}_\rho u(\ell) := \begin{cases} S^* D_\rho S u(\ell), & \ell \in \Omega_\Gamma, \\ D_\rho u(\ell), & \text{otherwise}. \end{cases} \tag{26}$$

The following lemma, proven in [5], is a straightforward extension of [9, Lemma 3.1].

LEMMA 3.3. *If the predictor u_0 is defined by* (21) *and $e(\ell)$ is given by* (25)*, then there exists a constant C such that*

$$|e_\sigma(\ell)| \le C|\sigma| \cdot |\ell|^{-1} \qquad \textit{and} \qquad |D_\rho e_\sigma(\ell)|_\gamma \le C|\rho| \cdot |\sigma| \cdot |\ell|^{-1}. \tag{27}$$

We now summarize our standing assumptions for dislocations:

D. $m = 2$, $d = 3$; $\Lambda = A\mathbb{Z}^m$; $P(\ell_1, \ell_2) = (\ell_1, \ell_2, \ell_3)$; u_0 is defined by (21); $y_0(\ell) = \ell + u_0(\ell)$.

Remark 3.4. One can treat antiplane models of pure screw dislocations by admitting displacements of the form $u_0 = (0, 0, u_{0,3})$ and $u = (0, 0, u_3)$. Similarly, one can treat the in-plane models of pure edge dislocations by admitting displacements of the form $u_0 = (u_{0,1}, u_{0,2}, 0)$ and $u = (u_1, u_2, 0)$ [9]. For antiplane models the atoms do not accumulate, and the condition **L** can be ignored.

3.2.5. Unified formulation. In order to consider the point defect and dislocation cases within a unified notation, we introduce the following notation. Let

$$u_0(\ell) := \begin{cases} 0 & \text{if } \mathbf{P}, \\ (21) & \text{if } \mathbf{D}, \end{cases} \qquad \mathsf{e}(\ell) := \begin{cases} \mathbf{0} & \text{if } \mathbf{P}, \\ e(\ell) & \text{if } \mathbf{D}, \end{cases} \qquad \text{and} \quad \mathsf{D}u(\ell) := \begin{cases} Du(\ell) & \text{if } \mathbf{P}, \\ \widetilde{D}u(\ell) & \text{if } \mathbf{D}. \end{cases}$$

Using the assumption $u_0 = 0$ in $\mathbf{P}$ for point defects and the slip invariance condition (24) for dislocations, we can rewrite the energy difference functional (19) as

$$\mathcal{E}(u) = \sum_{\ell \in \Lambda} \Big(V_\ell\big(\mathsf{e}(\ell) + \mathsf{D}u(\ell)\big) - V_\ell\big(\mathsf{e}(\ell)\big) \Big) \tag{28}$$

for both point defects and dislocations. The following result is proven in [5], extending an analogous result in [9] which is restricted to finite-range site energies.

LEMMA 3.5. *Suppose that* $\mathbf{P}$ *or* $\mathbf{D}$ *is satisfied; then* $\mathcal{E}$ *is well defined on* $\dot{\mathscr{W}}^{\mathrm{c}} \cap \mathrm{Adm}_0$*, where*

$$\dot{\mathscr{W}}^{\mathrm{c}} := \big\{ u : \Lambda \to \mathbb{R}^d \,\big|\, \exists R > 0 \text{ s.t. } u = \mathrm{const} \text{ in } \Lambda \setminus B_R \big\},$$

and continuous with respect to the $\dot{\mathscr{W}}^{1,2}$*-topology. Therefore, there exists a unique continuous extension to* $\dot{\mathscr{W}}^{1,2}$ *which belongs to* $C^{\mathrm{n}-1}(\dot{\mathscr{W}}^{1,2})$*.*

Having a well-defined energy-difference functional, the equilibrium state can be determined by solving the variational problem

$$\bar{u} \in \arg\min \big\{ \mathcal{E}(u), u \in \mathrm{Adm}_0 \big\}, \tag{29}$$

where "arg min" is understood in the sense of local minimality.

The next result is an extension of [9, Theorems 2.3 and 3.5], which gives the decay estimates for the equilibrium state for point defects and dislocations (see [5] for the proof).

THEOREM 3.6. *Let* $\Upsilon > 0$*. Suppose that either* $\mathbf{P}$ *or* $\mathbf{D}$ *is satisfied. If* $\bar{u} \in \mathrm{Adm}_0$ *is a strongly stable solution to* (29)*, that is,*

$$\exists\ \bar{c} > 0 \text{ s.t. } \big\langle \delta^2 \mathcal{E}(\bar{u}) v, v \big\rangle \geq \bar{c} \|Dv\|^2_{\ell^2_\Upsilon} \qquad \forall v \in \dot{\mathscr{W}}^{1,2}, \tag{30}$$

then there exist a constant $C > 0$ *and* $\bar{u}_\infty \in \mathbb{R}^d$ *such that*

$$|\mathsf{D}\bar{u}(\ell)|_\Upsilon \leq C(1 + |\ell|)^{-m} \log^t(2 + |\ell|), \tag{31}$$

$$|\bar{u}(\ell) - \bar{u}_\infty| \leq C(1 + |\ell|)^{1-m} \log^t(2 + |\ell|), \tag{32}$$

where $t = 0$ *for case* $\mathbf{P}$ *and* $t = 1$ *for case* $\mathbf{D}$*.*

Remark 3.7. The constants $\bar{c}, C$ in Theorem 3.6 have mild dependence on the parameter Υ. Nevertheless, since all norms $\|\cdot\|_{\ell^2_\gamma}$ are equivalent, we hereafter ignore this dependence.

Remark 3.8. It can be immediately seen that $|D\bar{u}(\ell)|_\Upsilon$ satisfies the same estimate as (31).

4. Energy-mixing.

4.1. Formulation of QM/MM energy mixing. Following the outline in section 2.1.1, we construct approximations to the TB site energy $V_\ell(\boldsymbol{g}) \approx V_\ell^{\rm MM}(\boldsymbol{g})$ for $\boldsymbol{g} \in (\mathbb{R}^m)^{\Lambda-\ell}$ by Taylor's expansion and approximate the energy difference functional by

$$\mathcal{E}(u) \approx \sum_{\ell\in\Lambda^{\rm QM}} \Big(V_\ell\big(\mathsf{e}(\ell)+\mathsf{D}u(\ell)\big)-V_\ell\big(\mathsf{e}(\ell)\big)\Big)+\sum_{\ell\in\Lambda^{\rm MM}} \Big(V_\ell^{\rm MM}\big(\mathsf{e}(\ell)+\mathsf{D}u(\ell)\big)-V_\ell^{\rm MM}\big(\mathsf{e}(\ell)\big)\Big). \tag{33}$$

Since minimizing (33) over $u \in \mathrm{Adm}_0$ is an infinite-dimensional problem, we will also approximate the space of trial functions.

4.1.1. Decomposition of Λ. We decompose the reference configuration Λ into three disjoint sets, $\Lambda = \Lambda^{\rm QM} \cup \Lambda^{\rm MM} \cup \Lambda^{\rm FF}$, where $\Lambda^{\rm QM}$ denotes the QM region, $\Lambda^{\rm MM}$ the MM region, and $\Lambda^{\rm FF}$ the *far-field* where atom positions will be frozen to those given by the far-field predictor. Moreover, we define a buffer region $\Lambda^{\rm BUF} \subset \Lambda^{\rm MM}$ surrounding $\Lambda^{\rm QM}$ such that all atoms in $\Lambda^{\rm BUF}$ are involved in the TB calculation when evaluating the site energies in $\Lambda^{\rm QM}$.

For simplicity, we use balls centered at the point defect or dislocation core to decompose Λ, and we use parameters $R_{\rm QM}$, $R_{\rm MM}$, and $R_{\rm BUF}$ to represent the respective radii, that is,

$$\Lambda^{\rm QM} = B_{R_{\rm QM}} \cap \Lambda, \qquad \Lambda^{\rm MM} = B_{R_{\rm MM}} \cap \Lambda \setminus \Lambda^{\rm QM}, \qquad \Lambda^{\rm BUF} = (B_{R_{\rm QM}+R_{\rm BUF}} \cap \Lambda) \setminus \Lambda^{\rm QM},$$

and $\Lambda^{\rm FF} = \Lambda \setminus (\Lambda^{\rm QM} \cup \Lambda^{\rm MM})$. See Figure 2 for a visualization of this decomposition.

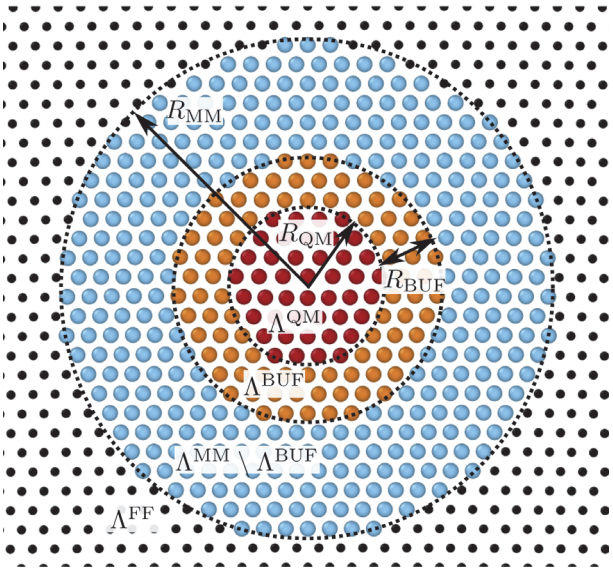

FIG. 2. *Decomposition of a crystal lattice with defect (edge dislocation) into QM, MM, buffer, and far-field regions, according to section* 4.1.1.

4.1.2. Buffered QM model and site energies. The site energies in the exact model have infinite range; hence we truncate them to obtain a computable approximation. To that end, we define

$$V_\ell^{\mathrm{BUF}}(\boldsymbol{g}) := \begin{cases} V_\ell^{\Lambda^{\mathrm{QM}}\cup\Lambda^{\mathrm{BUF}}}(\boldsymbol{g}), & \ell \in \Lambda^{\mathrm{QM}}, \\ V_\ell^{B_{R_{\mathrm{BUF}}}(\ell)}(\boldsymbol{g}), & \ell \in \Lambda^{\mathrm{MM}} \cup \Lambda^{\mathrm{FF}}, \end{cases} \tag{34}$$

where $V_\ell^\Omega(Du(\ell)) := E_\ell^\Omega(Px_0 + u)$.

We assume throughout that $R_{\mathrm{QM}} > R_{\mathrm{DEF}} + R_{\mathrm{BUF}}$. In this case, Theorem 3.1(ii)–(iii) and the assumptions on Λ in **P** and **D** imply that the truncated site potential (34) is independent of ℓ in $\Lambda^{\mathrm{MM}} \cup \Lambda^{\mathrm{FF}}$. That is, there exists $V_\#^{\mathrm{BUF}} : (\mathbb{R}^d)^{\mathcal{R}} \to \mathbb{R}$ such that

$$V_\ell^{\mathrm{BUF}}\big(Du(\ell)\big) = V_\#^{\mathrm{BUF}}\big(D_{\mathcal{R}}u(\ell)\big) \text{ with } \mathcal{R} = B_{R_{\mathrm{BUF}}} \cap (\Lambda \setminus 0),\ \forall\, \ell \in \Lambda^{\mathrm{MM}} \cup \Lambda^{\mathrm{FF}}. \tag{35}$$

Remark 4.1. We have used the buffer radius parameter R_{BUF} for both the buffer surrounding the QM region and for the buffer used in the approximate site potential V_ℓ^{BUF}. Although we could choose two separate parameters, they affect the error in similar ways; hence for simplicity of notation we use only one parameter.

4.1.3. QM/MM coupling. The homogeneity (35) allows us to construct the MM site potential by kth order Taylor expansion of $V_\#^{\mathrm{BUF}}$ about the far-field lattice state,

$$V^{\mathrm{MM}}(\boldsymbol{g}) := T_k V_\#^{\mathrm{BUF}}(\boldsymbol{g}) := V_\#^{\mathrm{BUF}}(\mathbf{0}) + \sum_{j=1}^{k} \frac{1}{j!} \delta^j V_\#^{\mathrm{BUF}}(\mathbf{0})\,[\boldsymbol{g}^{\otimes j}] \quad \text{with} \quad k \geq 2. \tag{36}$$

With the definitions (34) and (36) we can now specify the QM/MM energy-mixing scheme

$$\bar{u}^{\mathrm{H}} \in \arg\min\big\{\mathcal{E}^{\mathrm{H}}(u) \mid u \in \mathrm{Adm}_0^{\mathrm{H}}\big\}, \tag{37}$$

with the QM/MM hybrid energy difference functional

$$\begin{aligned} \mathcal{E}^{\mathrm{H}}(u) = &\sum_{\ell \in \Lambda^{\mathrm{QM}}} \Big(V_\ell^{\mathrm{BUF}}\big(\mathsf{e}(\ell) + \mathsf{D}u(\ell)\big) - V_\ell^{\mathrm{BUF}}\big(\mathsf{e}(\ell)\big) \Big) \\ &+ \sum_{\ell \in \Lambda^{\mathrm{MM}} \cup \Lambda^{\mathrm{FF}}} \Big(V^{\mathrm{MM}}\big(\mathsf{e}(\ell) + \mathsf{D}u(\ell)\big) - V^{\mathrm{MM}}\big(\mathsf{e}(\ell)\big) \Big) \end{aligned} \tag{38}$$

and admissible set

$$\mathrm{Adm}_{\mathfrak{m}}^{\mathrm{H}} := \mathrm{Adm}_{\mathfrak{m}} \cap \mathscr{W}^{\mathrm{H}}, \quad \text{where} \quad \mathscr{W}^{\mathrm{H}} := \Big\{ u \in \dot{\mathscr{W}}^{\mathrm{c}} \mid u = 0 \text{ in } \Lambda^{\mathrm{FF}} \Big\}. \tag{39}$$

Using same arguments as those in [5, 9], we have that $\mathcal{E}^{\mathrm{H}} \in C^{\mathfrak{n}-1}\big(\mathrm{Adm}_0^{\mathrm{H}}\big)$. Note, in particular, that the sum over $\Lambda^{\mathrm{MM}} \cup \Lambda^{\mathrm{FF}}$ in the definition of $\mathcal{E}^{\mathrm{H}}$ is in fact finite, since V^{MM} has a finite range of interaction.

We explain in detail in section 6 that the computational cost of higher order Taylor expansions is severe. It remains to be explored in future work whether MM site energies via Taylor expansions could be replaced with alternative approximations.

4.2. Error estimates. The QM/MM energy mixing scheme (37) satisfies the following approximation error estimate. The main steps of the proof are presented below, but some technical details are given in the appendices.

THEOREM 4.2. *Let* Υ *be given in Theorem* 3.6. *Suppose that either assumption* **P** *or* **D** *is satisfied and that* $\bar{u}$ *is a strongly stable solution of* (29).

If, in the definition of $\mathcal{E}^{\rm H}$ *in* (38), $V^{\rm MM}$ *is the* k*th order expansion in* (36) *and* $\mathfrak{n} \geq k+2$, *then there exist positive constants* C, κ, $c^{\rm QM}_{\rm BUF}$, $c^{\rm MM}_{\rm BUF}$ *such that, for* $R_{\rm QM}$ *sufficiently large and for*

$$R_{\rm BUF} \geq \max\{c^{\rm QM}_{\rm BUF} \log R_{\rm QM}, c^{\rm MM}_{\rm BUF} \log\log R_{\rm MM}\},$$

there exists a strongly stable solution $\bar{u}^{\rm H}$ *of* (37) *satisfying*

$$\|D\bar{u} - D\bar{u}^{\rm H}\|_{\ell^2_\Upsilon} \leq C\left(R_{\rm QM}^{-\alpha} + R_{\rm MM}^{-m/2}\log^t R_{\rm MM} + e^{-\kappa R_{\rm BUF}}\right) \quad \textit{and} \tag{40}$$

$$|\mathcal{E}(\bar{u}) - \mathcal{E}^{\rm H}(\bar{u}^{\rm H})| \leq C\left(R_{\rm QM}^{-\alpha-m/2}\log^t R_{\rm QM} + R_{\rm MM}^{-m}\log^{2t} R_{\rm MM} + e^{-\kappa R_{\rm BUF}}\right), \tag{41}$$

$$\textit{where} \quad \begin{cases} \alpha = (2k-1)m/2 & \textit{if } \mathbf{P}, \\ \alpha = k-1 & \textit{if } \mathbf{D}. \end{cases}$$

Proof. 1. *Quasi-best approximation.* Following [9, Lemma 7.3], we can construct $T^{\rm H}\bar{u} \in {\rm Adm}^{\rm H}_0$ by

$$T^{\rm H}\bar{u}(\ell) := \eta\big(\ell/R_{\rm MM}\big)\big(\bar{u}(\ell) - \bar{u}_\infty - a_{R_{\rm MM}}\big), \tag{42}$$

where $\bar{u}_\infty$ is given in Theorem 3.6, $a_{R_{\rm MM}} := \fint_{B_{5R_{\rm MM}/6}\setminus B_{4R_{\rm MM}/6}} \big(I\bar{u}(x) - \bar{u}_\infty\big)\,{\rm d}x$ with $I\bar{u}$ defined in section A, and $\eta \in C^1(\mathbb{R}^m)$ is a cutoff function satisfying $\eta(x) = 1$ for $|x| \leq 4/6$ and $\eta(x) = 0$ for $|x| \geq 5/6$. Then, for $R_{\rm MM}$ sufficiently large, we have from the decay estimates in Theorem 3.6 that

$$\|DT^{\rm H}\bar{u} - D\bar{u}\|_{\ell^2_\Upsilon} \leq C\|D\bar{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R_{\rm MM}/2})} \qquad \text{and} \tag{43}$$

$$|{\sf D}T^{\rm H}\bar{u}(\ell)|_\Upsilon \leq C(1+|\ell|)^{-m}\log^t(2+|\ell|) \quad \forall\, \ell \in \Lambda. \tag{44}$$

Let $r > 0$ be such that $B_r(\bar{u}) \subset {\rm Adm}_{\mathfrak{m}}$ for some $\mathfrak{m} > 0$. We have from Theorem 3.6 that, for $R_{\rm MM}$ sufficiently large, $T^{\rm H}\bar{u} \in B_{r/2}(\bar{u})$ and hence $B_{r/2}(T^{\rm H}\bar{u}) \subset {\rm Adm}_{\mathfrak{m}}$. Since $\mathcal{E} \in C^3({\rm Adm}_0)$, $\delta\mathcal{E}$ and $\delta^2\mathcal{E}$ are Lipschitz continuous in $B_r(\bar{u})$ with uniform Lipschitz constants L_1 and L_2; i.e.,

$$\|\delta\mathcal{E}(\bar{u}) - \delta\mathcal{E}(T^{\rm H}\bar{u})\| \leq L_1\|D\bar{u} - DT^{\rm H}\bar{u}\|_{\ell^2_\Upsilon} \leq CL_1\|D\bar{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R_{\rm MM}/2})} \qquad \text{and} \tag{45}$$

$$\|\delta^2\mathcal{E}(\bar{u}) - \delta^2\mathcal{E}(T^{\rm H}\bar{u})\| \leq L_2\|D\bar{u} - DT^{\rm H}\bar{u}\|_{\ell^2_\Upsilon} \leq CL_2\|D\bar{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R_{\rm MM}/2})}. \tag{46}$$

2. *Stability.* Since $\bar{u}$ is strongly stable, there exists $\bar{c} > 0$ such that $\langle\delta^2\mathcal{E}^{\rm H}(\bar{u})v, v\rangle \geq$

$\bar{c}\|Dv\|_{\ell^2_\Upsilon}^2$. For any $v \in \mathscr{W}^{\mathrm{H}}$, we have

$$
\begin{aligned}
&\langle \delta^2\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})v, v\rangle - \langle \delta^2\mathcal{E}(\bar{u})v, v\rangle \\
&= \big\langle \big(\delta^2\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}) - \delta^2\mathcal{E}(T^{\mathrm{H}}\bar{u})\big)v, v\big\rangle + \big\langle \big(\delta^2\mathcal{E}(T^{\mathrm{H}}\bar{u}) - \delta^2\mathcal{E}(\bar{u})\big)v, v\big\rangle \\
&= \sum_{\ell\in\Lambda} \Big\langle \Big(\delta^2 V_\ell^{\mathrm{BUF}}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big) - \delta^2 V_\ell\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big)\Big)\mathsf{D}v(\ell), \mathsf{D}v(\ell)\Big\rangle \\
&+ \sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}} \Big\langle \Big(\delta^2 V^{\mathrm{MM}}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big) - \delta^2 V_\ell^{\mathrm{BUF}}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big)\Big)\mathsf{D}v(\ell), \mathsf{D}v(\ell)\Big\rangle \\
&+ \big\langle \big(\delta^2\mathcal{E}(T^{\mathrm{H}}\bar{u}) - \delta^2\mathcal{E}(\bar{u})\big)v, v\big\rangle \qquad (47) =: Q_1 + Q_2 + Q_3.
\end{aligned}
$$

Using the estimate (93), we have

$$
|Q_1| \le C\sum_{\ell\in\Lambda} e^{-\eta R_{\mathrm{BUF}}}|\mathsf{D}v(\ell)|_\Upsilon^2 \le Ce^{-\eta R_{\mathrm{BUF}}}\|Dv\|_{\ell^2_\Upsilon}^2. \tag{48}
$$

Taylor's expansion (36) yields

$$
\begin{aligned}
|Q_2| = \sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}} &\Big\langle \Big(\delta^2 T_k V_{\#}^{\mathrm{BUF}}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big) \\
&\qquad -\delta^2 V_{\#}^{\mathrm{BUF}}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big)\Big)\mathsf{D}v(\ell), \mathsf{D}v(\ell)\Big\rangle \qquad (49) \\
\le C\sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}} &|\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)|_\Upsilon^{k-1}|\mathsf{D}v(\ell)|_\Upsilon^2 \;\le\; C\|\mathsf{e} + \mathsf{D}T^{\mathrm{H}}\bar{u}\|^{k-1}_{\ell^\infty_\Upsilon(\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}})}\|Dv\|^2_{\ell^2_\Upsilon}.
\end{aligned}
$$

The Lipschitz continuity (46) implies

$$
|Q_3| \le CL_2\|D\bar{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R_{\mathrm{MM}}/2})}\|Dv\|^2_{\ell^2_\Upsilon}. \tag{50}
$$

Using (44), (47), (48), (49), (50), the decay estimates in Lemma 3.3, Theorem 3.6, and the fact that $\bar{u}$ is a strongly stable solution, we have that for sufficiently large R_{QM} and R_{BUF} (note that $R_{\mathrm{MM}} \ge R_{\mathrm{QM}}$),

$$
\langle \delta^2\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})v, v\rangle \ge \frac{\bar{c}}{2}\|Dv\|^2_{\ell^2_\Upsilon}. \tag{51}
$$

3. *Consistency.* We estimate the consistency error, for any $v \in \mathscr{W}^{\mathrm{H}}$, by

$$
\begin{aligned}
&\big\langle \delta\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}), v\big\rangle \\
&\quad = \big\langle \delta\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}) - \delta\mathcal{E}(T^{\mathrm{H}}\bar{u}), v\big\rangle + \big\langle \delta\mathcal{E}(T^{\mathrm{H}}\bar{u}) - \delta\mathcal{E}(\bar{u}), v\big\rangle \\
&\quad = \sum_{\ell\in\Lambda} \big\langle \delta V_\ell^{\mathrm{BUF}}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big) - \delta V_\ell\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big), \mathsf{D}v(\ell)\big\rangle \\
&\qquad + \sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}} \big\langle \delta V^{\mathrm{MM}}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big) - \delta V_\ell^{\mathrm{BUF}}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)\big), \mathsf{D}v(\ell)\big\rangle \\
&\qquad + \big\langle \delta\mathcal{E}(T^{\mathrm{H}}\bar{u}) - \delta\mathcal{E}(\bar{u}), v\big\rangle \qquad (52) := T_1 + T_2 + T_3.
\end{aligned}
$$

The term T_1 can be estimated by

$$|T_1| \le Ce^{-\kappa R_{\rm BUF}} \|Dv\|_{\ell^2_\Upsilon}, \tag{53}$$

with some constant κ; a detailed proof of this assertion is presented in B.

To estimate T_2, we have from (36) that

$$\begin{aligned} |T_2| &= \sum_{\ell \in \Lambda^{\rm MM} \cup \Lambda^{\rm FF}} \big\langle \delta T_k V_\#^{\rm BUF}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\rm H}\bar{u}(\ell)\big) - \delta V_\#^{\rm BUF}\big(\mathsf{e}(\ell) + \mathsf{D}T^{\rm H}\bar{u}(\ell)\big), \mathsf{D}v(\ell)\big\rangle \\ &\le C \sum_{\ell \in \Lambda^{\rm MM} \cup \Lambda^{\rm FF}} |\mathsf{e}(\ell) + \mathsf{D}T^{\rm H}\bar{u}(\ell)|^k_\Upsilon |\mathsf{D}v(\ell)|_\Upsilon \\ &\le C\|\mathsf{e} + \mathsf{D}T^{\rm H}\bar{u}\|^k_{\ell^{2k}_\Upsilon(\Lambda^{\rm MM}\cup\Lambda^{\rm FF})} \|Dv\|_{\ell^2_\Upsilon}. \end{aligned} \tag{54}$$

Further, using (45), we can estimate T_3 by

$$|T_3| \le CL_1 \|D\bar{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R_{\rm MM}/2})} \|Dv\|_{\ell^2_\Upsilon}. \tag{55}$$

Taking into account (52), (53), (54), and (55), we have

$$\begin{aligned} &\big\langle \delta\mathcal{E}^{\rm H}(T^{\rm H}\bar{u}), v\big\rangle \\ &\quad \le C\left(e^{-\kappa R_{\rm BUF}} + \|\mathsf{e} + \mathsf{D}T^{\rm H}\bar{u}\|^k_{\ell^{2k}_\Upsilon(\Lambda^{\rm MM}\cup\Lambda^{\rm FF})} + \|D\bar{u}\|_{\ell^2_\Upsilon(\Lambda\setminus B_{R_{\rm MM}/2})}\right)\|Dv\|_{\ell^2_\Upsilon}. \end{aligned} \tag{56}$$

If **P** is satisfied, then we can obtain the estimates for point defects by substituting $\mathsf{e}(\ell) = \mathbf{0}$ and $|\mathsf{D}\bar{u}(\ell)|_\Upsilon \le C(1+|\ell|)^{-m}$ into (56):

$$\big|\big\langle \delta\mathcal{E}^{\rm H}(T^{\rm H}\bar{u}), v\big\rangle\big| \le C\left(R_{\rm QM}^{-(2k-1)m/2} + R_{\rm MM}^{-m/2} + e^{-\kappa R_{\rm BUF}}\right)\|Dv\|_{\ell^2_\Upsilon}. \tag{57}$$

If **D** is satisfied, then we can obtain the estimates for dislocations by substituting $\mathsf{e}(\ell) = e(\ell)$, $|e(\ell)|_\Upsilon \le C|\ell|^{-1}$, and $|\mathsf{D}\bar{u}(\ell)|_\Upsilon \le C(1+|\ell|)^{-2}\log(2+|\ell|)$ into (56):

$$\big|\big\langle \delta\mathcal{E}^{\rm H}(T^{\rm H}\bar{u}), v\big\rangle\big| \le C\left(R_{\rm QM}^{-k+1} + R_{\rm MM}^{-1}\log R_{\rm MM} + e^{-\kappa R_{\rm BUF}}\right)\|Dv\|_{\ell^2_\Upsilon}. \tag{58}$$

4. *Application of inverse function theorem.* With the stability (51) and consistency (56), we can apply the inverse function theorem [23, Lemma 2.2] to obtain, for $R_{\rm QM}, R_{\rm BUF}$ sufficiently large, the existence of a solution $\bar{u}^{\rm H}$ to (37), and the estimate

$$\|D\bar{u}^{\rm H} - DT^{\rm H}\bar{u}\|_{\ell^2_\Upsilon} \le C\begin{cases} R_{\rm QM}^{-(2k-1)m/2} + R_{\rm MM}^{-m/2} + e^{-\kappa R_{\rm BUF}} & \text{if } \mathbf{P}, \\ R_{\rm QM}^{-k+1} + R_{\rm MM}^{-1}\log R_{\rm MM} + e^{-\kappa R_{\rm BUF}} & \text{if } \mathbf{D}, \end{cases} \tag{59}$$

which together with (43) completes the proof of (40). The error estimate, together with the stability estimate (51), in particular, imply that, for $R_{\rm QM}, R_{\rm BUF}$ sufficiently large, $\bar{u}^{\rm H}$ is strongly stable.

5. *Error in the energy.* Next, we estimate the error in the energy difference functional. From $\mathcal{E} \in C^2(\mathrm{Adm}_0)$ we have that

$$\begin{aligned} \big|\mathcal{E}(T^{\rm H}\bar{u}) - \mathcal{E}(\bar{u})\big| &= \Big|\int_0^1 \big\langle \delta\mathcal{E}\big((1-s)\bar{u} + sT^{\rm H}\bar{u}\big), T^{\rm H}\bar{u} - \bar{u}\big\rangle \,{\rm d}s\Big| \\ &= \Big|\int_0^1 \big\langle \delta\mathcal{E}\big((1-s)\bar{u} + sT^{\rm H}\bar{u}\big) - \delta\mathcal{E}(\bar{u}), T^{\rm H}\bar{u} - \bar{u}\big\rangle \,{\rm d}s\Big| \le C\|DT^{\rm H}\bar{u} - D\bar{u}\|^2_{\ell^2_\Upsilon}, \end{aligned} \tag{60}$$

and from $\mathcal{E}^{\rm H} \in C^2(\mathrm{Adm}_0^{\rm H})$ we have that

$$\big|\mathcal{E}^{\rm H}(\bar{u}^{\rm H}) - \mathcal{E}^{\rm H}(T^{\rm H}\bar{u})\big| \le C\|D\bar{u}^{\rm H} - DT^{\rm H}\bar{u}\|_{\ell^2_\Upsilon}^2. \tag{61}$$

Denoting $g(\ell) = \mathsf{D}T^{\rm H}\bar{u}(\ell)$ and suppressing the argument (ℓ) in $g(\ell)$ and $\mathsf{e}(\ell)$, we have

$$\begin{aligned}
&|\mathcal{E}(T^{\rm H}\bar{u}) - \mathcal{E}^{\rm H}(T^{\rm H}\bar{u})| \\
&= \sum_{\ell\in\Lambda} \big(V_\ell(g+\mathsf{e}) - V_\ell(\mathsf{e}) - V_\ell^{\rm BUF}(g+\mathsf{e}) + V_\ell^{\rm BUF}(\mathsf{e})\big) \\
&\quad + \sum_{\ell\in\Lambda^{\rm MM}\cup\Lambda^{\rm FF}} \big(V_\#^{\rm BUF}(g+\mathsf{e}) - V_\#^{\rm BUF}(\mathsf{e}) - T_k V_\#^{\rm BUF}(g+\mathsf{e}) + T_k V_\#^{\rm BUF}(\mathsf{e})\big) \\
&:= S_1 + S_2, \qquad (62)
\end{aligned}$$

where S_1 is estimated in B by

$$|S_1| \le Ce^{-\kappa R_{\rm BUF}}, \tag{63}$$

and S_2 is estimated by

$$\begin{aligned}
|S_2| &\le \sum_{\ell\in\Lambda^{\rm MM}\cup\Lambda^{\rm FF}} \Big(\frac{1}{(k+1)!}\big(\delta^{k+1}V_\#^{\rm BUF}(0)(g+\mathsf{e})^{\otimes k+1} - \delta^{k+1}V_\#^{\rm BUF}(0)\mathsf{e}^{\otimes k+1}\big) \\
&\qquad + C\big(|g+\mathsf{e}|_\Upsilon^{k+2} + |\mathsf{e}|_\Upsilon^{k+2}\big)\Big) \\
&\le C \sum_{\ell\in\Lambda^{\rm MM}\cup\Lambda^{\rm FF}} \Big(|g|_\Upsilon(|g+\mathsf{e}|_\Upsilon^k + |\mathsf{e}|_\Upsilon^k) + |g+\mathsf{e}|_\Upsilon^{k+2} + |\mathsf{e}|_\Upsilon^{k+2}\Big) \\
&\le C\Big(\||\mathsf{D}T^{\rm H}\bar{u}(\ell)|_\Upsilon \cdot |\mathsf{e}(\ell) + \mathsf{D}T^{\rm H}\bar{u}(\ell)|_\Upsilon^k\|_{\ell^1_\Upsilon(\Lambda^{\rm MM}\cup\Lambda^{\rm FF})} \\
&\qquad + \||\mathsf{e}(\ell) + \mathsf{D}T^{\rm H}\bar{u}(\ell)|_\Upsilon^{k+2}\|_{\ell^1_\Upsilon(\Lambda^{\rm MM}\cup\Lambda^{\rm FF})}\Big) \\
&\le C \begin{cases} R_{\rm QM}^{-km} & \text{if } \mathbf{P}, \\ R_{\rm QM}^{-k}\log R_{\rm QM} & \text{if } \mathbf{D}. \end{cases} \qquad (64)
\end{aligned}$$

Taking (59)–(64) into account, we have

$$\begin{aligned}
|\mathcal{E}^{\rm H}(\bar{u}^{\rm H}) - \mathcal{E}(\bar{u})| &\le |\mathcal{E}^{\rm H}(\bar{u}^{\rm H}) - \mathcal{E}^{\rm H}(T^{\rm H}\bar{u})| + |\mathcal{E}^{\rm H}(T^{\rm H}\bar{u}) - \mathcal{E}(T^{\rm H}\bar{u})| + |\mathcal{E}(T^{\rm H}\bar{u}) - \mathcal{E}(\bar{u})| \\
&\le C \begin{cases} R_{\rm QM}^{-km} + R_{\rm MM}^{-m} + e^{-\kappa R_{\rm BUF}} & \text{if } \mathbf{P}, \\ R_{\rm QM}^{-k}\log R_{\rm QM} + R_{\rm MM}^{-2}\log^2 R_{\rm MM} + e^{-\kappa R_{\rm BUF}} & \text{if } \mathbf{D}, \end{cases} \qquad (65)
\end{aligned}$$

which completes the proof of (41). ∎

5. Force-mixing.

5.1. Formulation of QM/MM force mixing. To construct a force-based QM/MM coupling scheme, we follow the idea in section 2.2.1. In the MM region we construct an approximation to the TB force $F_\ell(y) \approx F_\ell^{\rm MM}(y)$ by Taylor's expansion in order to ensure a good match between the QM and MM models.

Our starting point, instead of the energy minimization formulation (29), is the force-equilibrium formulation

$$\text{Find } \bar{u} \in \mathrm{Adm}_0, \quad \text{s.t.} \quad F_\ell(y_0 + \bar{u}) = 0 \quad \forall\, \ell \in \Lambda, \tag{66}$$

where

$$F_\ell(y_0+u) = \sum_{\rho\in\ell-\Lambda} V_{\ell-\rho,\rho}\big(Du_0(\ell-\rho)+Du(\ell-\rho)\big) - \sum_{\rho\in\Lambda-\ell} V_{\ell,\rho}\big(Du_0(\ell)+Du(\ell)\big). \tag{67}$$

We have from (19) and Theorem 3.2(iv) that $F(y_0+u) = \nabla\mathcal{E}(u)$; hence any solution of (29) also solves (67).

To simplify the notation in the construction of the QM/MM scheme, we define

$$\mathcal{F}_\ell^\Omega(u) := F_\ell^\Omega(y_0+u) \qquad \text{and} \qquad \widetilde{\mathcal{F}}_\ell^\Omega(w) := F_\ell^\Omega(Px_0+w),$$

and we remark that

$$\widetilde{\mathcal{F}}_\ell^\Omega(u_0+u) = \mathcal{F}_\ell^\Omega(u) = \sum_{\rho\in\ell-\Omega} V^\Omega_{\ell-\rho,\rho}\big(Du_0(\ell-\rho)+Du(\ell-\rho)\big) - \sum_{\rho\in\Omega-\ell} V^\Omega_{\ell,\rho}\big(Du_0(\ell)+Du(\ell)\big). \tag{68}$$

We decompose the reference configuration into Λ^{QM}, Λ^{MM}, Λ^{FF}, Λ^{BUF} in the same way as in section 4. To obtain computable forces we then truncate the force of the infinite lattice,

$$\mathcal{F}_\ell^{\mathrm{BUF}}(u) := \begin{cases} \mathcal{F}_\ell^{\Lambda^{\mathrm{QM}}\cup\Lambda^{\mathrm{BUF}}}(u), & \ell \in \Lambda^{\mathrm{QM}}, \\ \mathcal{F}_\ell^{B_{R_{\mathrm{BUF}}}(\ell)}(u), & \ell \in \Lambda^{\mathrm{MM}} \cup \Lambda^{\mathrm{FF}}. \end{cases} \tag{69}$$

If $R_{\mathrm{QM}} > R_{\mathrm{DEF}} + R_{\mathrm{BUF}}$, then Theorem 3.2(ii)–(iii) and the assumptions on Λ in **P** and **D** imply that the truncated force operator $\widetilde{\mathcal{F}}_\ell^{B_{R_{\mathrm{BUF}}}(\ell)}$ is independent of ℓ in $\Lambda^{\mathrm{MM}} \cup \Lambda^{\mathrm{FF}}$. That is, there exists $\mathcal{F}_\#^{\mathrm{BUF}} : (\mathbb{R}^m)^{\mathcal{R}} \to \mathbb{R}$, where $\mathcal{R} = (A\mathbb{Z}^m) \cap B_{R_{\mathrm{BUF}}}$ such that

$$\widetilde{\mathcal{F}}_\ell^{B_{R_{\mathrm{BUF}}}(\ell)}(v) = \mathcal{F}_\#^{\mathrm{BUF}}\left(v(\cdot-\ell)|_{B_{R_{\mathrm{BUF}}}}\right) \qquad \forall\, \ell \in \Lambda^{\mathrm{MM}} \cup \Lambda^{\mathrm{FF}}. \tag{70}$$

We now define the MM force to be the kth order Taylor expansion of $\mathcal{F}_\#^{\mathrm{BUF}}$,

$$\mathcal{F}_\#^{\mathrm{MM}}(w) \;:=\; T_k\mathcal{F}_\#^{\mathrm{BUF}}(w) \;:=\; \mathcal{F}_\#^{\mathrm{BUF}}(0) + \sum_{j=1}^{k} \frac{1}{j!}\delta^j\mathcal{F}_\#^{\mathrm{BUF}}(0)\left[w^{\otimes j}\right] \text{ with } \; k \geq 1. \tag{71}$$

We remark that the zeroth-order term in the expansion vanishes since the reference lattice is an equilibrium.

We have the following force-mixing QM/MM coupling model:

$$\text{Find } \bar{u}^{\mathrm{H}} \in \mathrm{Adm}_0^{\mathrm{H}}, \quad \text{s.t.} \quad \mathcal{F}_\ell^{\mathrm{H}}\big(\bar{u}^{\mathrm{H}}\big) = 0 \qquad \forall\, \ell \in \Lambda^{\mathrm{QM}} \cup \Lambda^{\mathrm{MM}} \tag{72}$$

with the hybrid force

$$\mathcal{F}_\ell^{\mathrm{H}}(u) = \begin{cases} \mathcal{F}_\ell^{\mathrm{BUF}}(u), & \ell \in \Lambda^{\mathrm{QM}}, \\ \mathcal{F}_\#^{\mathrm{MM}}\left(\big(u_0(\cdot-\ell)+u(\cdot-\ell)\big)|_{B_{R_{\mathrm{BUF}}}(\ell)}\right), & \ell \in \Lambda^{\mathrm{MM}}. \end{cases} \tag{73}$$

We emphasize that $\mathcal{F}^{\mathrm{H}}$ is not a gradient of any energy functional. For $v : \Lambda \to \mathbb{R}$, we will use the notation $\langle \mathcal{F}^{\mathrm{H}}(u), v\rangle := \sum_{\ell\in\Lambda^{\mathrm{QM}}\cup\Lambda^{\mathrm{MM}}} \mathcal{F}_\ell^{\mathrm{H}}(u)\cdot v(\ell)$ in our analysis.

5.2. Error estimates.

THEOREM 5.1. *Let* Υ *be given in Theorem* 3.6. *Suppose that either assumption* **P** *or* **D** *is satisfied and that* $\bar{u}$ *is a strongly stable solution of* (66).

Suppose that, in the definition of $\mathcal{F}^{\mathrm{H}}$ *in* (73), $\mathcal{F}^{\mathrm{MM}}_{\#}$ *is the* k*th order expansion in* (71) *and* $\mathfrak{n} \geq k+3$. *Then, for any given MM region growth constant* $C^{\mathrm{MM}}_{\mathrm{QM}} > 0$, *there exist positive constants* C, κ, $c^{\mathrm{QM}}_{\mathrm{BUF}}$, $c^{\mathrm{MM}}_{\mathrm{BUF}}$ *such that, if* R_{QM} *is sufficiently large, while* $R_{\mathrm{QM}}, R_{\mathrm{BUF}}, R_{\mathrm{MM}}$ *maintain the bounds*

$$\log \frac{R_{\mathrm{MM}}}{R_{\mathrm{QM}}} \leq C^{\mathrm{MM}}_{\mathrm{QM}} \qquad \textit{and} \qquad R_{\mathrm{BUF}} \geq \max\{c^{\mathrm{QM}}_{\mathrm{BUF}} \log R_{\mathrm{MM}}, c^{\mathrm{MM}}_{\mathrm{BUF}} \log\log R_{\mathrm{MM}}\},$$

there exists a strongly stable solution $\bar{u}^{\mathrm{H}}$ *of* (72) *satisfying*

$$\|D\bar{u} - D\bar{u}^{\mathrm{H}}\|_{\ell^2_\Upsilon} \leq C\left(R^{-\alpha}_{\mathrm{QM}} \log R_{\mathrm{MM}} + R^{-m/2}_{\mathrm{MM}} \log^t R_{\mathrm{MM}} + e^{-\kappa R_{\mathrm{BUF}}}\right), \tag{74}$$

$$\textit{where} \quad \begin{cases} \alpha = (2k+1)m/2 & \textit{if } \mathbf{P}, \\ \alpha = k & \textit{if } \mathbf{D}. \end{cases}$$

Remark 5.2. In view of the bound $\log \frac{R_{\mathrm{MM}}}{R_{\mathrm{QM}}} \leq C^{\mathrm{MM}}_{\mathrm{QM}}$, we could replace $\log R_{\mathrm{MM}}$ with $\log R_{\mathrm{QM}}$ in (74); however, we keep $\log R_{\mathrm{MM}}$ to highlight the dependence of the error estimate on the growth of R_{MM} relative to R_{QM}.

Proof. We will follow the same strategy as in the proof of Theorem 4.2.

1. *Quasi-best approximation.* We take the approximation $T^{\mathrm{H}}\bar{u} \in \mathrm{Adm}^{\mathrm{H}}_0$ constructed in the proof of Theorem 4.2, so that the properties from (43)–(46) are satisfied.

2. *Stability.* Let $\mathcal{E}^{\mathrm{H}}$ be defined by (38) with V^{MM} being the $(k+1)$th order expansion in (36). For any $v \in \mathscr{W}^{\mathrm{H}}$, we have

$$\left\langle \delta\mathcal{F}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})v, v\right\rangle = \left\langle \big(\delta\mathcal{F}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}) - \delta^2\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})\big)v, v\right\rangle + \left\langle \delta^2\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})v, v\right\rangle, \tag{75}$$

where the first term is estimated in Appendix C as

$$\left|\left\langle \big(\delta\mathcal{F}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}) - \delta^2\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})\big)v, v\right\rangle\right| \leq C\left(R^{-k+3/4}_{\mathrm{QM}} + e^{-\kappa R_{\mathrm{BUF}}}\right)\|Dv\|^2_{\ell^2_\Upsilon} \tag{76}$$

with some constant κ, and the second term is estimated in section 4 (51). Therefore, we have that for sufficiently large R_{QM}, R_{MM}, and R_{BUF},

$$\left\langle \delta\mathcal{F}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})v, v\right\rangle \geq \frac{\bar{c}}{4}\|Dv\|^2_{\ell^2_\Upsilon}. \tag{77}$$

3. *Consistency.* We estimate the consistency error for any $v \in \mathscr{W}^{\mathrm{H}}$:

$$\left\langle \mathcal{F}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}), v\right\rangle = \left\langle \delta\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}), v\right\rangle + \left\langle \mathcal{F}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}) - \delta\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}), v\right\rangle, \tag{78}$$

where the first term has been estimated in section 4 and the second term can be written as

$$\begin{aligned}
&\left\langle \mathcal{F}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}) - \delta\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}), v\right\rangle \\
&\quad = \sum_{\ell \in \Lambda^{\mathrm{QM}} \setminus \Lambda^{\mathrm{I}}} \big(\mathcal{F}^{\mathrm{H}}_\ell(T^{\mathrm{H}}\bar{u}) - \nabla_\ell\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})\big)v(\ell) + \sum_{\ell \in \Lambda^{\mathrm{I}}} \big(\mathcal{F}^{\mathrm{H}}_\ell(T^{\mathrm{H}}\bar{u}) - \nabla_\ell\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})\big)v(\ell) \\
&\quad + \sum_{\ell \in \Lambda^{\mathrm{MM}} \setminus \Lambda^{\mathrm{I}}} \big(\mathcal{F}^{\mathrm{H}}_\ell(T^{\mathrm{H}}\bar{u}) - \nabla_\ell\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})\big)v(\ell) \\
&\quad := P_1 + P_2 + P_3
\end{aligned} \tag{79}$$

with the interface region $\Lambda^{\rm I} := \{\ell \in \Lambda,\ R_{\rm QM} - R_{\rm BUF} \le |\ell| \le R_{\rm QM} + R_{\rm BUF}\}$.

To estimate P_1, we have from the expressions (68) that for any $\ell \in \Lambda^{\rm QM}\backslash\Lambda^{\rm I}$,

$$\begin{aligned}
&\mathcal{F}_\ell^{\rm H}(T^{\rm H}\bar{u}) - \nabla_\ell \mathcal{E}^{\rm H}(T^{\rm H}\bar{u}) \\
&= \sum_{\ell-\rho\in\Lambda^{\rm BUF}} \Big(V_{\ell-\rho,\rho}^{\Lambda^{\rm QM}\cup\Lambda^{\rm BUF}}\big(Du_0(\ell-\rho) + DT^{\rm H}\bar{u}(\ell-\rho)\big) \\
&\quad - V_{\ell-\rho,\rho}^{\rm MM}\big(Du_0(\ell-\rho) + DT^{\rm H}\bar{u}(\ell-\rho)\big)\Big) \\
&\quad - \sum_{\ell+\rho\in\Lambda^{\rm BUF}} \Big(V_{\ell,\rho}^{\Lambda^{\rm QM}\cup\Lambda^{\rm BUF}}\big(Du_0(\ell) + DT^{\rm H}\bar{u}(\ell)\big) - V_{\ell,\rho}^{\rm MM}\big(Du_0(\ell) + DT^{\rm H}\bar{u}(\ell)\big)\Big) \\
&\le Ce^{-\eta R_{\rm BUF}},
\end{aligned} \tag{80}$$

with some constant η, where Theorem 3.1(i) is used for the last inequality. Then we have from Lemma A.2 that when $R_{\rm BUF} > \frac{4}{\eta}\log R_{\rm QM}$ and $R_{\rm BUF} > \frac{4}{\eta}\log\log R_{\rm MM}$,

$$P_1 \le Ce^{-\frac{\eta}{4}R_{\rm BUF}}\|Dv\|_{\ell^2_\Upsilon}. \tag{81}$$

To estimate P_2, we have

$$\begin{aligned}
&|\mathcal{F}_\ell^{\rm H}(T^{\rm H}\bar{u}) - \nabla_\ell \mathcal{E}^{\rm H}(T^{\rm H}\bar{u})| \\
&\le |\mathcal{F}_\ell^{\rm BUF}(T^{\rm H}\bar{u}) - \mathcal{F}_\ell(T^{\rm H}\bar{u})| + |\nabla_\ell \mathcal{E}(T^{\rm H}\bar{u}) - \nabla_\ell \mathcal{E}^{\rm H}(T^{\rm H}\bar{u})| \\
&\le C\Big(e^{-\eta R_{\rm BUF}} + \sum_{\ell-\rho\in B_{R_{\rm BUF}}(\ell)\cap\Lambda^{\rm MM}} e^{-\eta|\rho|}\cdot|\mathsf{e}(\ell-\rho) + \mathsf{D}T^{\rm H}\bar{u}(\ell-\rho)|_\Upsilon^{k+1}\Big)
\end{aligned}$$

for $\ell \in \Lambda^{\rm I}\cap\Lambda^{\rm QM}$ and

$$\begin{aligned}
&|\mathcal{F}_\ell^{\rm H}(T^{\rm H}\bar{u}) - \nabla_\ell \mathcal{E}^{\rm H}(T^{\rm H}\bar{u})| \\
&\le |\mathcal{F}_\ell^{\rm H}(T^{\rm H}\bar{u}) - \mathcal{F}_\ell^{\rm BUF}(T^{\rm H}\bar{u})| + |\mathcal{F}_\ell^{\rm BUF}(T^{\rm H}\bar{u}) - \mathcal{F}_\ell(T^{\rm H}\bar{u})| + |\nabla_\ell \mathcal{E}(T^{\rm H}\bar{u}) - \nabla_\ell \mathcal{E}^{\rm H}(T^{\rm H}\bar{u})| \\
&\le C\Big(e^{-\eta R_{\rm BUF}} + \sum_{\ell-\rho\in B_{R_{\rm BUF}}(\ell)\cap\Lambda^{\rm MM}} e^{-\eta|\rho|}\cdot|\mathsf{e}(\ell-\rho) + \mathsf{D}T^{\rm H}\bar{u}(\ell-\rho)|_\Upsilon^{k+1}\Big)
\end{aligned}$$

for $\ell \in \Lambda^{\rm I}\cap\Lambda^{\rm MM}$. Let $\Lambda^{\rm I'} := \{\ell \in \Lambda,\ R_{\rm QM} - R_{\rm BUF} \le |\ell| \le R_{\rm QM} + 2R_{\rm BUF}\}$. If **P** is satisfied, then we have from Theorem 3.6 and Lemma A.2 that

$$\begin{aligned}
P_2 &\le C\sum_{\ell\in\Lambda^{\rm I'}}\Big(e^{-\eta R_{\rm BUF}} + |\ell|^{-m(k+1)}\Big)\Big(\sum_{|\rho|\le R_{\rm BUF}} e^{-\eta|\rho|}\cdot|v(\ell+\rho)|\Big) \\
&\le C\|Dv\|_{\ell^2_\Upsilon}\begin{cases} \log R_{\rm MM}\cdot R_{\rm BUF}\cdot\Big(R_{\rm QM}^{-2k-1} + R_{\rm QM}\cdot e^{-\eta R_{\rm BUF}}\Big) & \text{if } m=2, \\ R_{\rm BUF}^{5/6}\cdot\Big(R_{\rm QM}^{-3k-4/3} + R_{\rm QM}^{5/3}\cdot e^{-\eta R_{\rm BUF}}\Big) & \text{if } m=3. \end{cases}
\end{aligned} \tag{82}$$

If **D** is satisfied, then

$$\begin{aligned}
P_2 &\le C\sum_{\ell\in\Lambda^{\rm I'}}\Big(e^{-\eta R_{\rm BUF}} + |\ell|^{-(k+1)}\Big)\Big(\sum_{|\rho|\le R_{\rm BUF}} e^{-\eta|\rho|}\cdot|v(\ell+\rho)|\Big) \\
&\le C\log R_{\rm MM}\cdot R_{\rm BUF}\cdot\Big(R_{\rm QM}^{-k} + R_{\rm QM}\cdot e^{-\eta R_{\rm BUF}}\Big)\|Dv\|_{\ell^2_\Upsilon}.
\end{aligned} \tag{83}$$

To estimate P_3, let $\widetilde{\mathcal{F}}_\ell(v) := F_\ell(Px_0 + v)$ and $\widetilde{\mathcal{E}}(v) := \sum_{\ell\in\Lambda}\big(E_\ell(Px_0+v) - E_\ell(Px_0)\big)$. Define

$$T_k\widetilde{\mathcal{F}}_\ell(w) = \nabla_\ell T_{k+1}\widetilde{\mathcal{E}}(w) := \frac{\partial T_{k+1}\widetilde{\mathcal{E}}(w)}{\partial w_\ell}. \tag{84}$$

Then, for any $\ell \in \Lambda^{\mathrm{MM}}\backslash\Lambda^{\mathrm{I}}$, we have

$$\begin{aligned}
&|\mathcal{F}_\ell^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}) - \nabla_\ell\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})|\\
&\le |\mathcal{F}_\ell^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}) - T_k\widetilde{\mathcal{F}}_\ell(u_0 + T^{\mathrm{H}}\bar{u})| + |\nabla_\ell T_{k+1}\widetilde{\mathcal{E}}(u_0+T^{\mathrm{H}}\bar{u}) - \nabla_\ell\mathcal{E}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u})|\\
&\le \begin{cases} Ce^{-\eta R_{\mathrm{BUF}}}|\ell|^{-m} & \text{if } \mathbf{P},\\ Ce^{-\eta R_{\mathrm{BUF}}}|\ell|^{-2}\log|\ell| & \text{if } \mathbf{D}, \end{cases}
\end{aligned}$$

where the same arguments as those in Lemma B.3 are used to derive the last inequality. Then we have from Lemma A.2 that when $R_{\mathrm{BUF}} > \frac{4}{\eta}\log R_{\mathrm{QM}}$ and $R_{\mathrm{BUF}} > \frac{6}{\eta}\log\log R_{\mathrm{MM}}$,

$$P_3 \le Ce^{-\frac{\eta}{4}R_{\mathrm{BUF}}}\|Dv\|_{\ell^2_\Upsilon}. \tag{85}$$

Taking (78), (79), (81), (82), (83), (85) and the estimates (57), (58) with order $k+1$ into account, we have the consistency

$$|\langle\mathcal{F}^{\mathrm{H}}(T^{\mathrm{H}}\bar{u}), v\rangle| \le C\|Dv\|_{\ell^2_\Upsilon}\begin{cases} R_{\mathrm{QM}}^{-(2k+1)m/2}\log R_{\mathrm{MM}} + R_{\mathrm{MM}}^{-m/2} + e^{-\frac{\eta}{4}R_{\mathrm{BUF}}} & \text{if } \mathbf{P},\\ R_{\mathrm{QM}}^{-k}\log R_{\mathrm{MM}} + R_{\mathrm{MM}}^{-1}\log R_{\mathrm{MM}} + e^{-\frac{\eta}{4}R_{\mathrm{BUF}}} & \text{if } \mathbf{D} \end{cases} \tag{86}$$

when $R_{\mathrm{BUF}} > \frac{4}{\eta}\log R_{\mathrm{QM}}$ and $R_{\mathrm{BUF}} > \frac{4}{\eta}\log\log R_{\mathrm{MM}}$.

4. *Application of inverse function theorem.* With the stability (77) and consistency (86), we can apply the inverse function theorem [23, Lemma 2.2] to obtain the existence of $\bar{u}^{\mathrm{H}}$ and the estimate

$$\|D\bar{u}^{\mathrm{H}} - D\bar{u}\|_{\ell^2_\Upsilon} \le \begin{cases} C\Big(R_{\mathrm{QM}}^{-(2k+1)m/2}\log R_{\mathrm{MM}} + R_{\mathrm{MM}}^{-m/2} + e^{-\kappa R_{\mathrm{BUF}}}\Big) & \text{if } \mathbf{P},\\ C\Big(R_{\mathrm{QM}}^{-k}\log R_{\mathrm{MM}} + R_{\mathrm{MM}}^{-1}\log R_{\mathrm{MM}} + e^{-\kappa R_{\mathrm{BUF}}}\Big) & \text{if } \mathbf{D} \end{cases} \tag{87}$$

with some constant κ. This completes the proof. ∎

6. Concluding remarks. In this paper, we construct new QM/MM coupling algorithms for crystalline solids with embedded defects, based on either energy-mixing or force-mixing formulations. Unlike in commonly used QM/MM schemes, our approach does not employ "off-the-shelf" interatomic potentials (or forces) but constructs a potential (or force) specifically for the coupling with the QM model. The accuracy of our algorithms (with respect to increasing QM region size) is quantified by rigorous convergence rates.

In the energy-based QM/MM coupling methods, with a given size R_{QM} of the QM region, we observe from Theorem 4.2 that one should take $R_{\mathrm{MM}} \approx R_{\mathrm{QM}}^{\alpha/\beta}$ (e.g., in the case $\mathbf{P}$, $k=2$, $R_{\mathrm{MM}} \approx R_{\mathrm{QM}}^3$) and $R_{\mathrm{BUF}} \approx \log R_{\mathrm{QM}}$ to balance the errors. With these choices, we obtain the errors in Table 1, written in terms of R_{QM}, dropping logarithmic contributions, and writing the order of expansion as $k = k_{\mathrm{E}}$.

TABLE 1

Choice of $R_{\rm MM}$ and error with respect to $R_{\rm QM}$ for QM/MM schemes, with MM potential order $k = k_{\rm E}$ for the energy based scheme and $k = k_{\rm F}$ for the force-based scheme. The energy error applies only for energy-mixing schemes.

	Case **P**, $m = 2$			Case **P**, $m = 3$			Case **D**		
$k_{\rm E}$	2	3	4	2	3	4	2	3	4
$k_{\rm F}$	1	2	3	1	2	3	1	2	3
$R_{\rm MM}$	$R_{\rm QM}^3$	$R_{\rm QM}^5$	$R_{\rm QM}^7$	$R_{\rm QM}^3$	$R_{\rm QM}^5$	$R_{\rm QM}^7$	$R_{\rm QM}$	$R_{\rm QM}^2$	$R_{\rm QM}^3$
error	$R_{\rm QM}^{-3}$	$R_{\rm QM}^{-5}$	$R_{\rm QM}^{-7}$	$R_{\rm QM}^{-4.5}$	$R_{\rm QM}^{-7.5}$	$R_{\rm QM}^{-10.5}$	$R_{\rm QM}^{-1}$	$R_{\rm QM}^{-2}$	$R_{\rm QM}^{-3}$
E-error	$R_{\rm QM}^{-4}$	$R_{\rm QM}^{-6}$	$R_{\rm QM}^{-8}$	$R_{\rm QM}^{-6}$	$R_{\rm QM}^{-9}$	$R_{\rm QM}^{-12}$	$R_{\rm QM}^{-2}$	$R_{\rm QM}^{-3}$	$R_{\rm QM}^{-4}$

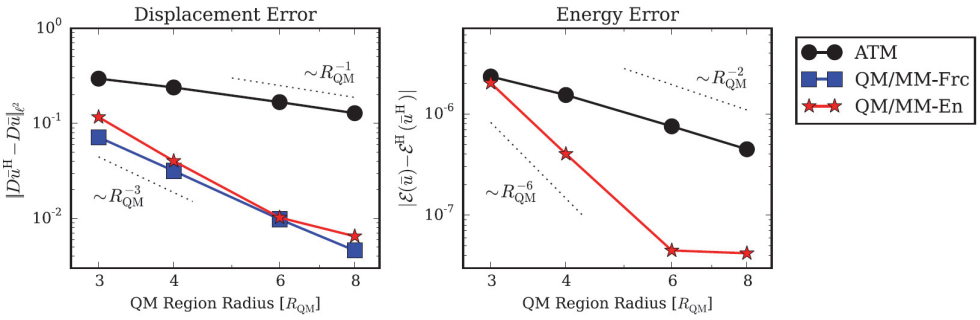

FIG. 3. *Numerical verification of the convergence rates predicted in Theorems* 4.2 *and* 5.1 *(ATM denotes a pure QM scheme as described in* [6]*). The results are consistent with the theory, but the numerical rate for the energy is better than our analytical prediction. (See* [9] *for a similar gap in the theory.) The inconsistency in the rates in the last data point in the energy error, and to some extent also visible in the displacement error for QM-MM-En, is likely due to a buffer radius that is chosen slightly too small for this level of accuracy.*

In our force-mixing QM/MM scheme, we obtain precisely the same rates and hence the same balance of approximation parameters, except that the order of expansion in the force is one less than that of the energy in our energy-mixing scheme. The rates are also shown in Table 1, with $k = k_{\rm F}$.

We note in particular that, for point defects, the QM/MM hybrid scheme achieves dramatic rates of convergence, already for a second order expansion of the site energies, respectively, first order expansion of the forces ($k_{\rm E} = 2, k_{\rm F} = 1$). By contrast, for dislocations, the second order expansion is no better than pure QM "clamped boundary condition" calculations (see [6, section 4.2] and [9]). Only higher order expansions ($k_{\rm E} \geq 3$, $k_{\rm F} \geq 2$) of the site energy will give improved rates of convergence for hybrid QM/MM simulation of dislocations.

To limit the scope of the present work we will address the challenges in the implementation of both schemes in a separate paper in full detail, but we present a preliminary numerical test. Using the TB toy model from [6, sec. 5], the same simulation setup (2D triangular lattice with a di-vacancy defect), $k_{\rm E} = 2$, $k_{\rm F} = 1$, buffer radii $R_{\rm BUF} = 1 + 0.6 \log(R_{\rm QM})$, and MM domain radii $R_{\rm MM} = \frac{1}{2} R_{\rm QM}^3 + 2R_{\rm BUF}$, we numerically obtain the results displayed in Figure 3. This test should only be considered as a motivation for further study, but its implementation allows us to make the following observations.

(1) A particular challenge in our schemes is the computational cost of higher order expansions, which is of the order $O\big((R_{\rm BUF})^{km}\big)$. For example, taking only up

to third nearest neighbors in an FCC lattice ($R_{\rm BUF}/R_{\rm NN} \approx 1.7$, where $R_{\rm NN}$ is the nearest-neighbor distance) results in 42 neighboring atoms, which would result in over 2M expansion coefficients at third order, and over 250M expansion coefficients at fourth order. We will exploit lattice symmetries to reduce the number of expansion coefficients that need to be calculated. The fact that the order of expansion is lower in force-based schemes, without loss of accuracy, is a significant advantage.

(2) The computation of the kth order expansion of the site energies requires kth order perturbation theory (or finite differences). By contrast, the computation of forces and their derivatives can take advantage of the $2n+1$-*theorem*; hence expanding the forces is computationally much cheaper than expanding energies, even at the same order of expansion. An analogous comment applies to the computation of the QM region contribution to the hybrid forces or gradient of the hybrid energy.

We conclude by commenting that, in view of the computational cost associated with Taylor expansions as site energies, alternative approaches may be required. Our analysis, or variations thereof, can then still be applied as long as the MM model is tuned to interact "correctly" with the QM model.

Appendix A. Interpolation of lattice functions. For each $u : \Lambda \to \mathbb{R}^d$, we denote its continuous and piecewise affine interpolant with respect to $\mathcal{T}_\Lambda$ by Iu, and its piecewise constant gradient by ∇Iu. For simplicity, we will abuse the notation and write $\nabla u \equiv \nabla Iu$ whenever possible without confusion. We have the following lemma from [24, 25].

LEMMA A.1. *If $v \in \dot{\mathscr{W}}^{1,2}$, then there exist constants c and C such that*

$$c\|\nabla v\|_{L^2} \le \|Dv\|_{\ell^2_\gamma} \le C\|\nabla v\|_{L^2}. \tag{88}$$

The following auxiliary results are useful in our analysis in that they sometimes allow us to avoid stress-strain ("weak") representations of residual forces that we need to estimate.

LEMMA A.2. (i) *If $m = 2$, then there exists $C > 0$ such that*

$$|v(\ell) - v(m)| \le C\|Dv\|_{\ell^2_\gamma}\big(1 + \log|\ell - m|\big) \qquad \forall v \in \dot{\mathscr{W}}^{1,2}, \quad \ell, m \in \Lambda.$$

(ii) *If $m = 3$, then there exists $C > 0$ such that, for each $v \in \dot{\mathscr{W}}^{1,2}$ there exists $v_\infty \in \mathbb{R}^d$ such that*

$$\|v - v_\infty\|_{\ell^6} \le C\|Dv\|_{\ell^2}.$$

Proof. The result is a straightforward generalization of [24, Proposition 12(ii)–(iii)]. ∎

LEMMA A.3. *Let $m = 2$, $0 < L < R$, and $v : \Lambda \to \mathbb{R}$ satisfy $v(\ell) = 0 \ \forall\ |\ell| \ge R$. If $f : \Lambda \to \mathbb{R}$ satisfies $|f(\ell)| \le c|\ell|^{-2}$, then there exists a constant C such that*

$$\sum_{L \le |\ell| \le R} f(\ell) \cdot v(\ell) \le C \log^{3/2}\left(\frac{R}{L}\right) \cdot \|Dv\|_{\ell^2_\gamma} \qquad \forall\ v \in \mathscr{W}^{\rm H}. \tag{89}$$

Proof. For simplicity of notation let $r := |\mathbf{r}|, \hat{\mathbf{r}} = \mathbf{r}/r$ and $v = Iv$. Let $R' \ge R$, minimally, such that $v = 0$ in $B^{\rm c}_{R'}$. For each $T \in \mathcal{T}_\Lambda, T \subset B_{R'} \setminus B_L$ we have

$$\begin{aligned}\Big|\sum_{\ell \in \Lambda \cap T} f(\ell) \cdot v(\ell)\Big| &\le \max_{\ell \in \Lambda \cap T} |f(\ell)| \sum_{\ell \in \Lambda \cap T} |v(\ell)| \le C \max_{\ell \in \Lambda \cap T} |\ell|^{-2} \int_T |Iv(\mathbf{r})|\, \mathrm{d}\mathbf{r} \\ &\le C \int_T r^{-2} |Iv(\mathbf{r})|\, \mathrm{d}\mathbf{r}.\end{aligned}$$

Therefore, it follows that

$$\left| \sum_{L \le |\ell| \le R} f(\ell) \cdot v(\ell) \right| \le C \int_{B_{R'} \setminus B_L} \frac{|Iv(\mathbf{r})|}{r^2} \, \mathrm{d}\mathbf{r}. \tag{90}$$

We have from the estimate

$$|v(\mathbf{r})| = \left| \int_r^{R'} \frac{d}{dt} v(t\hat{\mathbf{r}}) \, \mathrm{d}t \right| \le \int_r^{R'} |\nabla v(t\hat{\mathbf{r}})| \, \mathrm{d}t$$

that

$$\begin{aligned}
\int_{B_{R'} \setminus B_L} \frac{|v(\mathbf{r})|}{r^2} \, \mathrm{d}\mathbf{r} &= \int_{S^{m-1}} \int_{r=L}^{R'} r^{-1} |v(r\hat{\mathbf{r}})| \, \mathrm{d}r \, \mathrm{d}\hat{\mathbf{r}} \le \int_{S^{m-1}} \int_{r=L}^{R'} r^{-1} \int_{t=r}^{R'} |\nabla v(t\hat{\mathbf{r}})| \, \mathrm{d}t \, \mathrm{d}r \, \mathrm{d}\hat{\mathbf{r}} \\
&= \int_{S^{m-1}} \int_{t=L}^{R'} |\nabla v(t\hat{\mathbf{r}})| \int_{r=L}^{t} r^{-1} \, \mathrm{d}r \, \mathrm{d}t \, \mathrm{d}\hat{\mathbf{r}} \\
&= \int_{S^{m-1}} \int_{t=L}^{R'} t^{1/2} |\nabla v(t\hat{\mathbf{r}})| t^{-1/2} \log \frac{t}{L} \, \mathrm{d}t \, \mathrm{d}\hat{\mathbf{r}} \\
&\le \|\nabla v\|_{L^2(B_{R'} \setminus B_L)} \Big(\int_{S^{m-1}} \int_{t=L}^{R'} t^{-1} \log^2(t/L) \, \mathrm{d}t \, \mathrm{d}\hat{\mathbf{r}} \Big)^{1/2} \\
&\le C \log^{3/2} \left(\frac{R'}{L} \right) \|\nabla v\|_{L^2}.
\end{aligned}$$

Applying Lemma A.1 and (90), noting that $\log(R'/R) \le C$, completes the proof. ∎

Appendix B. Estimates of buffer truncations. Recall that the assumptions we placed on the hamiltonian are a special case of those employed in [6]. The following lemma therefore follows immediately from [6, (3.10)–(3.12)].

LEMMA B.1. *Let $\ell \in M \subsetneq N \subset \Lambda$, $u \in \mathrm{Adm}_0(\Lambda)$, $0 \le j \le \mathfrak{n} - 1$, and $\boldsymbol{\rho} = (\rho_1, \dots, \rho_j) \in (M - \ell)^j$. Then there exist positive constants C and η, depending on $\mathfrak{m}$, such that*

$$\left| V_{\ell,\boldsymbol{\rho}}^M \big(Du(\ell)\big) - V_{\ell,\boldsymbol{\rho}}^N \big(Du(\ell)\big) \right| \le C e^{-\eta \left(\mathrm{dist}(\ell, N \setminus M) + \sum_{i=1}^j |\rho_i| \right)} \tag{91}$$

with $\mathrm{dist}(\ell, \Omega) = \min_{k \in \Omega} \{|\ell - k|\}$. *Moreover, we have*

$$\left| V_{\ell,\boldsymbol{\rho}}^M \big(Du(\ell)\big) - V_{\ell,\boldsymbol{\rho}} \big(Du(\ell)\big) \right| \le C e^{-\eta \left(\mathrm{dist}(\ell, \Lambda \setminus M) + \sum_{i=1}^j |\rho_i| \right)}. \tag{92}$$

A direct consequence of Lemma B.1 is

$$\left| V_{\ell,\boldsymbol{\rho}} \big(Du(\ell)\big) - V_{\ell,\boldsymbol{\rho}}^{\mathrm{BUF}} \big(Du(\ell)\big) \right| \le C e^{-\eta R_{\mathrm{BUF}}} \tag{93}$$

for $y \in \mathcal{V}_{\mathfrak{m}}(\Lambda)$ and $\boldsymbol{\rho} = (\rho_1, \dots, \rho_j) \in (\Lambda - \ell)^j$ with $0 \le j \le \mathfrak{n} - 1$, $\max_i |\rho_i| \le R_{\mathrm{BUF}}$.

For $y \in \mathcal{V}_{\mathfrak{m}}$, $\ell \in \Lambda^{\mathrm{MM}} \cup \Lambda^{\mathrm{FF}}$ and $R > 0$, we define $V_\ell^R \big(Du(\ell)\big) := V_\ell^{B_R(\ell) \setminus B_{R_{\mathrm{DEF}}}} \cdot \big(Du(\ell)\big)$. Therefore, we have

$$V_{\ell,\rho}^R \big(Du(\ell)\big) := \begin{cases} 0 & \text{if } |\rho| > R \text{ or } \ell + \rho \in \Lambda \cap B_{R_{\mathrm{DEF}}}, \\ V_{\ell,\rho}^{B_R(\ell) \setminus B_{R_{\mathrm{DEF}}}} \big(Du(\ell)\big) & \text{otherwise.} \end{cases} \tag{94}$$

The difference between V_ℓ and V_ℓ^R can be estimated using Lemma B.1: If $R < |\ell| - R_{\mathrm{DEF}}$, $0 \le j \le \mathfrak{n} - 1$, and $\boldsymbol{\rho} \in (\Lambda - \ell)^j$ with $\max_i |\rho_i| \le R$, then there exist constants C and η such that

$$\left| V_{\ell,\boldsymbol{\rho}} \big(Du(\ell)\big) - V_{\ell,\boldsymbol{\rho}}^R \big(Du(\ell)\big) \right| \le C e^{-\eta \left(R + \sum_{i=1}^j |\rho_i| \right)}. \tag{95}$$

The next lemma establishes the homogeneity of the site energy V_ℓ^R.

LEMMA B.2. *Let $\ell, k \in \Lambda$ and $R < \min\{|\ell|, |k|\} - R_{\rm DEF}$. If $u, u' \in \mathrm{Adm}_0(\Lambda)$ satisfy $D_\rho u(\ell) = D_\rho u'(k)$ for all $|\rho| < R$, then*

$$V_\ell^R\big(Du(\ell)\big) = V_k^R\big(Du'(k)\big) \qquad \text{and} \qquad V_{\ell,\boldsymbol{\rho}}^R\big(Du(\ell)\big) = V_{k,\boldsymbol{\rho}}^R\big(Du'(k)\big) \tag{96}$$

for $\boldsymbol{\rho} \in (A\mathbb{Z}^m \cap B_R - 0)^j$, $\max_i |\rho_i| < R$.

Proof. Using the condition $\{D_\rho u(\ell)\}_{|\rho|<R} = \{D_\rho u'(k)\}_{|\rho|<R}$ and Theorem 3.1(ii) with $g(x) = x - x(\ell) + x(k)$, (iii) with $\mathcal{G}(x) = x - \ell + k$, we can derive $V_\ell^R\big(Du(\ell)\big) = V_k^R\big(Du'(k)\big)$. Then the second part of (96) is a direct consequence. ∎

Before the proof of (53), we need the following estimate for $V_{\ell,\rho}^{\rm A} - V_{\#,\rho}^{\rm BUF}$ on the predictor, where the auxiliary site potential $V_\ell^{\rm A}$ is defined by

$$V_\ell^{\rm A}(\mathbf{g}) := \begin{cases} V_\ell^{|\ell|-R_{\rm DEF}}(\mathbf{g}) & \text{if } |\ell| \le 3R_{\rm QM}, \\ V_\ell^{\frac{|\ell|}{3}}(\mathbf{g}) & \text{if } |\ell| > 3R_{\rm QM}, \end{cases} \qquad \text{for } \mathbf{g} \in \big(\mathbb{R}^d\big)^{\Lambda-\ell}.$$

LEMMA B.3. *Let $R_{\rm BUF} > \max\{\frac{4}{\eta}\log R_{\rm QM}, \frac{6}{\eta}\log\log R_{\rm MM}\}$, where η is the constant from Lemma* B.1. *If the assumption* **P** *or* **D** *is satisfied, then there exists a constant C such that*

$$\sum_{\ell\in\Lambda^{\rm MM}\cup\Lambda^{\rm FF}} \big\langle \delta V_{\#}^{\rm BUF}\big(\mathsf{e}(\ell)\big) - \delta V_\ell^{\rm A}\big(\mathsf{e}(\ell)\big), \mathsf{D}v(\ell)\big\rangle \le Ce^{-\frac{\eta}{4}R_{\rm BUF}}\|Dv\|_{\ell^2_\gamma} \quad \forall v \in \mathscr{W}^{\rm H}. \tag{97}$$

Proof. The left-hand side of (97) can be written in the form

$$\sum_{\ell\in\Lambda^{\rm MM}\cup\Lambda^{\rm FF}} \sum_{\rho\in\Lambda-\ell} \big(V_{\#,\rho}^{\rm BUF}\big(Du_0(\ell)\big) - V_{\ell,\rho}^{\rm A}\big(Du_0(\ell)\big)\big)\big(v(\ell+\rho) - v(\ell)\big) \tag{98}$$

$$:= \sum_{R_{\rm QM}-R_{\rm DEF}\le|\ell|\le 3R_{\rm QM}} \big(\tilde f^{\rm A}(\ell) - \tilde f^{\rm BUF}(\ell)\big)v(\ell) + \sum_{|\ell|>3R_{\rm QM}} \big(f^{\rm A}(\ell) - f^{\rm BUF}(\ell)\big)v(\ell),$$

where $f^{\rm A}(\ell)$ and $\tilde f^{\rm A}(\ell)$ are given in terms of $V_{\ell,\rho}^{\rm A}(Du_0(\ell))$ and $f^{\rm BUF}(\ell)$ and $\tilde f^{\rm BUF}(\ell)$ are given in terms of $V_{\ell,\rho}^{\rm BUF}(Du_0(\ell))$. The precise forms of $\tilde f^{\rm A}(\ell)$ and $\tilde f^{\rm BUF}(\ell)$ are not important; we can obtain from Lemma B.1 and the fact that they are given in terms of $V_{\ell,\rho}^{\rm A}(Du_0(\ell))$ and $V_{\ell,\rho}^{\rm BUF}(Du_0(\ell))$ that

$$\Big|\tilde f^{\rm A}(\ell) - \tilde f^{\rm BUF}(\ell)\Big| \le Ce^{-\eta R_{\rm BUF}} \quad \text{for } R_{\rm QM} - R_{\rm DEF} \le |\ell| \le 3R_{\rm QM}. \tag{99}$$

When $|\ell| > 3R_{\rm QM}$, we have

$$f^{\rm BUF}(\ell) = \sum_{\rho\in A\mathbb{Z}^d-0,\ |\rho|\le R_{\rm BUF}} \big(V_{\ell-\rho,\rho}^{\rm BUF}\big(Du_0(\ell-\rho)\big) - V_{\ell,\rho}^{\rm BUF}\big(Du_0(\ell)\big)\big) \text{ and} \tag{100}$$

$$\begin{aligned} f^{\rm A}(\ell) &= \sum_{\rho\in A\mathbb{Z}^d-0,\ |\rho|\le\frac{|\ell|}{3}} \big(V_{\ell-\rho,\rho}^{\rm A}\big(Du_0(\ell-\rho)\big) - V_{\ell,\rho}^{\rm A}\big(Du_0(\ell)\big)\big) \\ &= \sum_{\rho\in A\mathbb{Z}^d-0,\ |\rho|\le\frac{|\ell|}{3}} \Big(V_{\ell-\rho,\rho}^{\rm A}\big(Du_0(\ell-\rho)\big) - V_{\ell-\rho,\rho}^{\frac{|\ell|}{3}}\big(Du_0(\ell-\rho)\big)\Big) \\ &\quad + \sum_{\rho\in A\mathbb{Z}^d-0,\ |\rho|\le\frac{|\ell|}{3}} \Big(V_{\ell-\rho,\rho}^{\frac{|\ell|}{3}}\big(Du_0(\ell-\rho)\big) - V_{\ell,\rho}^{\frac{|\ell|}{3}}\big(Du_0(\ell)\big)\Big) \end{aligned}$$

$$:= f_a(\ell) + f_b(\ell). \tag{101}$$

Lemma B.1 and the definition of V_ℓ^{A} imply that

$$f_a \le Ce^{-\frac{2}{9}\eta|\ell|}. \tag{102}$$

If **P** is satisfied, then we have from $u_0(\ell-\rho)=u_0(\ell)=0$ and Lemma B.2 that

$$f_b(\ell)=0 \qquad \text{and} \qquad f^{\mathrm{BUF}}(\ell)=0. \tag{103}$$

If **D** is satisfied, we first consider the left half-space $\ell_1<\hat{x}_1$, in which case we can replace D by D. Letting $e=Du_0(\ell)$ and suppressing the argument (ℓ), we have from Lemma B.2 and the expansion

$$V_{,\rho}(e)=V_{,\rho}(\mathbf{0})+\big\langle \delta V_{,\rho}(\mathbf{0}),e\big\rangle+\frac{1}{2}\int_0^1(1-t)\big\langle \delta^2V_{,\rho}(te)e,e\big\rangle\,\mathrm{d}t \text{ with } V=V_\ell^{\frac{|\ell|}{3}} \text{ or } V_{\#}^{\mathrm{BUF}} \tag{104}$$

that

$$\begin{aligned} f_b(\ell)-f^{\mathrm{BUF}}(\ell)&=\sum_{\rho,\xi}\left(V_{\ell,\rho\xi}^{\frac{|\ell|}{3}}(\mathbf{0})-V_{\#,\rho\xi}^{\mathrm{BUF}}(\mathbf{0})\right)D_{-\rho}e_\xi \\ &\quad+\frac{1}{2}\int_0^1(1-t)D_{-\rho}\left\langle\Big(\delta^2V_{\ell,\rho}^{\frac{|\ell|}{3}}(te)-\big(\delta^2V_{\#,\rho}^{\mathrm{BUF}}(te)\big)\Big)e,e\right\rangle\,\mathrm{d}t:=F_1+F_2. \end{aligned} \tag{105}$$

Using Lemmas 3.3 and B.1, we have

$$F_1\le Ce^{-\eta R_{\mathrm{BUF}}}|\ell|^{-2} \qquad \text{and} \qquad F_2\le Ce^{-\eta R_{\mathrm{BUF}}}|\ell|^{-2},$$

which implies $|f_b(\ell)-f^{\mathrm{BUF}}(\ell)|\le Ce^{-\eta R_{\mathrm{BUF}}}|\ell|^{-2}$ for $\ell_1<\hat{x}_1$. For the right half-space $\ell_1>\hat{x}_1$, we can repeat the foregoing argument to deduce

$$\big|S\left(f_b(\ell)-f^{\mathrm{BUF}}(\ell)\right)\big|\le Ce^{-\eta R_{\mathrm{BUF}}}|\ell|^{-2}.$$

Note that S is an $O(1)$ shift, which implies $|f_b(\ell)-f^{\mathrm{BUF}}(\ell)|\le Ce^{-\eta R_{\mathrm{BUF}}}|\ell|^{-2}$ for $\ell_1>\hat{x}_1$.

Taking (100), (101), (102), (103), and the above estimates for $|f_b(\ell)-f^{\mathrm{BUF}}(\ell)|$ into account, we have

$$\big|f^{\mathrm{A}}(\ell)-f^{\mathrm{BUF}}(\ell)\big|\le C\left(e^{-\frac{2}{9}\eta|\ell|}+e^{-\eta R_{\mathrm{BUF}}}|\ell|^{-2}\right) \qquad \text{for } \ |\ell|>3R_{\mathrm{QM}}. \tag{106}$$

Combining (98), (99), (106), and $v\in\mathscr{W}^{\mathrm{H}}$ yields

$$\sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}}\big\langle\delta V_{\#}^{\mathrm{BUF}}\big(\mathsf{e}(\ell)\big)-\delta V_\ell^{\mathrm{A}}\big(\mathsf{e}(\ell)\big),\mathsf{D}v(\ell)\big\rangle=\sum_{R_{\mathrm{QM}}-R_{\mathrm{DEF}}\le|\ell|\le R_{\mathrm{MM}}}\mathfrak{f}(\ell)v(\ell) \tag{107}$$

$$\text{with}|\mathfrak{f}(\ell)|\le\begin{cases} Ce^{-\eta R_{\mathrm{BUF}}} & \text{if } R_{\mathrm{QM}}-R_{\mathrm{DEF}}\le|\ell|\le 3R_{\mathrm{QM}},\\ C\left(e^{-\frac{2}{9}\eta|\ell|}+e^{-\eta R_{\mathrm{BUF}}}|\ell|^{-2}\right) & \text{if } |\ell|>3R_{\mathrm{QM}}.\end{cases} \tag{108}$$

Since $R_{\mathrm{BUF}}>\frac{4}{\eta}\log R_{\mathrm{QM}}$, we can write $|\mathfrak{f}(\ell)|\le Ce^{-\frac{\eta}{2}R_{\mathrm{BUF}}}|\ell|^{-2}$, which together with Lemma A.3 completes the proof of (97) as $R_{\mathrm{BUF}}>\frac{6}{\eta}\log\log R_{\mathrm{MM}}$. ∎

Proof of (53). Denoting $g(\ell)=\mathsf{D}T^{\mathrm{H}}\bar{u}(\ell)$ and suppressing the argument (ℓ) in $g(\ell)$ and $\mathsf{e}(\ell)$, we have from Lemmas B.1 and B.3 that

$$\begin{aligned} &\sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}}\big\langle\delta V_{\#}^{\mathrm{BUF}}\big(\mathsf{e}+g\big)-\delta V_\ell^{\mathrm{A}}\big(\mathsf{e}+g\big),\mathsf{D}v(\ell)\big\rangle=\sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}}\big\langle\delta V_{\#}^{\mathrm{BUF}}\big(\mathsf{e}\big)-\delta V_\ell^{\mathrm{A}}\big(\mathsf{e}\big),\mathsf{D}v(\ell)\big\rangle\\ &\quad+\sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}}\int_0^1(1-t)\left\langle\Big(\delta^2V_{\#}^{\mathrm{BUF}}\big(\mathsf{e}+tg\big)-\delta^2V_\ell^{\mathrm{A}}\big(\mathsf{e}+tg\big)\Big)g,\mathsf{D}v(\ell)\right\rangle\,\mathrm{d}t\\ &\quad\le C\left(e^{-\frac{\eta}{4}R_{\mathrm{BUF}}}+e^{-\eta R_{\mathrm{BUF}}}\|g\|_{\ell^2_\Upsilon}\right)\|Dv\|_{\ell^2_\Upsilon}. \end{aligned} \tag{109}$$

Using (93), (95), (109), and Theorem 3.6, we have

$$\begin{aligned} T_1 &= \sum_{\ell\in\Lambda^{\mathrm{QM}}} \big\langle \delta V_\ell^{\mathrm{BUF}}\big(\mathsf{e}+g\big) - \delta V_\ell\big(\mathsf{e}+g\big), \mathsf{D}v(\ell)\big\rangle \\ &\quad + \sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}} \big\langle \delta V_\#^{\mathrm{BUF}}\big(\mathsf{e}+g\big) - \delta V_\ell^{\mathrm{A}}\big(\mathsf{e}+g\big), \mathsf{D}v(\ell)\big\rangle \\ &\quad + \sum_{\ell\in\Lambda^{\mathrm{MM}}\cup\Lambda^{\mathrm{FF}}} \big\langle \delta V_\ell^{\mathrm{A}}\big(\mathsf{e}+g\big) - \delta V_\ell\big(\mathsf{e}+g\big), \mathsf{D}v(\ell)\big\rangle \\ &\le C\big(R_{\mathrm{QM}}^{m/2} e^{-\eta R_{\mathrm{BUF}}} + e^{-\frac{\eta}{4}R_{\mathrm{BUF}}} + e^{-\frac{\eta}{4}R_{\mathrm{QM}}}\big)\|Dv\|_{\ell^2_\Upsilon}, \end{aligned} \tag{110}$$

which completes the proof since $R_{\mathrm{QM}}^{m/2} e^{-\eta R_{\mathrm{BUF}}}$ and $e^{-\frac{\eta}{4}R_{\mathrm{QM}}}$ can be omitted compared with the middle term when $R_{\mathrm{BUF}} > \frac{m}{2\eta}\log R_{\mathrm{QM}}$. ∎

Proof of (63). Using $T^{\mathrm{H}}\bar{u} \in \mathrm{Adm}_0^{\mathrm{H}}$ and the expansion

$$V(\mathsf{e}+g) = V(\mathsf{e}) + \big\langle \delta V(\mathsf{e}), g\big\rangle + \frac{1}{2}\int_0^1 (1-t)\big\langle \delta^2 V(\mathsf{e}+tg)g, g\big\rangle \,\mathrm{d}t \tag{111}$$

$$\text{with } V = V_\ell \text{ or } V_\ell^{\mathrm{BUF}}$$

for $R_{\mathrm{QM}} \le |\ell| \le R_{\mathrm{MM}} + R_{\mathrm{BUF}}$, we have

$$\begin{aligned} |S_1| \le & \sum_{\ell\in\Lambda^{\mathrm{QM}}} \big(V_\ell(g+\mathsf{e}) - V_\ell(\mathsf{e}) - V_\ell^{\mathrm{BUF}}(g+\mathsf{e}) + V_\ell^{\mathrm{BUF}}(\mathsf{e})\big) \\ & + \sum_{R_{\mathrm{QM}}\le|\ell|\le R_{\mathrm{MM}}+R_{\mathrm{BUF}}} \big\langle \delta V_\ell(\mathsf{e}) - \delta V_\ell^{\mathrm{BUF}}(\mathsf{e}), g\big\rangle \\ & + \frac{1}{2}\sum_{R_{\mathrm{QM}}\le|\ell|\le R_{\mathrm{MM}}+R_{\mathrm{BUF}}} \int_0^1 (1-t)\,\big\langle \big(\delta^2 V_\ell(\mathsf{e}+tg) - \delta^2 V_\ell^{\mathrm{BUF}}(\mathsf{e}+tg)\big)g, g\big\rangle \,\mathrm{d}t \end{aligned}$$

$(112) := S_1^a + S_1^b + S_1^c$.

The first and third groups of (112) can be estimated by Lemma B.1:

$$|S_1^a| \le C R_{\mathrm{QM}}^{m/2} e^{-\eta R_{\mathrm{BUF}}} \qquad \text{and} \qquad |S_1^c| \le C e^{-\eta R_{\mathrm{BUF}}}\|g\|^2_{\ell^2_\Upsilon}. \tag{113}$$

Using Lemma B.3, we can obtain the estimate for the second group:

$$|S_1^b| \le C e^{-\frac{\eta}{4}R_{\mathrm{BUF}}} \qquad \text{when } R_{\mathrm{BUF}} > \frac{6}{\eta}\log\log R_{\mathrm{MM}},$$

which together with (112) and (113) completes the proof of (63). ∎

Appendix C. Stability of force-mixing methods. Here, we establish the result that the energy-mixing Hessian and force-mixing Jacobian are "close." This result is reminiscent of similar results in the context of atomistic/continuum blending [19], but the proofs are not closely related.

Proof of (76). Let $\Lambda^{\rm I} := \{\ell \in \Lambda,\ R_{\rm QM} - R_{\rm BUF} \le |\ell| \le R_{\rm QM} + R_{\rm BUF}\}$ be the interface region. Denoting $\widetilde{\mathcal{F}}^{\rm b}_\ell(v) := \widetilde{\mathcal{F}}^{B_{R_{\rm BUF}}(\ell)}_\ell(v)$ and $\widetilde{\mathcal{E}}^{\rm b}(v) := \sum_{\ell\in\Lambda}\big(E^{\rm buf}_\ell(Px_0 + v) - E^{\rm BUF}_\ell(Px_0)\big)$ with $E^{\rm BUF}_\ell = E^{B_{R_{\rm BUF}}(\ell)}_\ell$, we can split

$$
\begin{aligned}
&\big\langle\big(\delta\mathcal{F}^{\rm H}(T^{\rm H}\bar u) - \delta^2\mathcal{E}^{\rm H}(T^{\rm H}\bar u)\big)v, v\big\rangle = \sum_{\ell\in\Lambda}\big\langle\delta\mathcal{F}^{\rm H}_\ell(T^{\rm H}\bar u) - \delta\nabla_\ell\mathcal{E}^{\rm H}(T^{\rm H}\bar u), v\big\rangle v(\ell)\\
&= \sum_{\ell\in A\mathbb{Z}^m}\big\langle\delta\widetilde{\mathcal{F}}^{\rm b}_\ell(0) - \delta\nabla_\ell\widetilde{\mathcal{E}}^{\rm b}(0), v\big\rangle v(\ell)\\
&+ \sum_{\ell\in\Lambda^{\rm QM}\setminus\Lambda^{\rm I}}\big\langle\delta\mathcal{F}^{\rm H}_\ell(T^{\rm H}\bar u) - \delta\nabla_\ell\mathcal{E}^{\rm H}(T^{\rm H}\bar u), v\big\rangle v(\ell)\\
&- \sum_{\ell\in A\mathbb{Z}^d\cap B_{R_{\rm QM}-R_{\rm BUF}}}\big\langle\delta\widetilde{\mathcal{F}}^{\rm b}_\ell(0) - \delta\nabla_\ell\widetilde{\mathcal{E}}^{\rm b}(0), v\big\rangle v(\ell)\\
&+ \sum_{\ell\in\Lambda^{\rm I}}\Big(\big\langle\delta\mathcal{F}^{\rm H}_\ell(T^{\rm H}\bar u) - \delta\widetilde{\mathcal{F}}^{\rm b}_\ell(0), v\big\rangle v(\ell) - \big\langle\delta\nabla_\ell\mathcal{E}^{\rm H}(T^{\rm H}\bar u) - \delta\nabla_\ell\widetilde{\mathcal{E}}^{\rm b}(0), v\big\rangle v(\ell)\Big)\\
&+ \sum_{\ell\in\Lambda^{\rm MM}\setminus\Lambda^{\rm I}}\Big(\big\langle\delta\mathcal{F}^{\rm H}_\ell(T^{\rm H}\bar u) - \delta\widetilde{\mathcal{F}}^{\rm b}_\ell(0), v\big\rangle v(\ell) - \big\langle\delta\nabla_\ell\mathcal{E}^{\rm H}(T^{\rm H}\bar u) - \delta\nabla_\ell\widetilde{\mathcal{E}}^{\rm b}(0), v\big\rangle v(\ell)\Big)
\end{aligned}
$$

$(114) := Q_1 + Q_2 + Q_3 + Q_4 + Q_5$.

Estimate for Q_1. Using Theorem 3.2(ii), (iii) and [15, Lemma 3.4], we can rewrite Q_1 as

$$
Q_1 = \sum_{\ell\in A\mathbb{Z}^d}\sum_{\rho\in A\mathbb{Z}^d - 0} D_\rho v(\ell)^{\rm T}\big(A^F_\rho - A^E_\rho\big)D_\rho v(\ell) \tag{115}
$$

with $A^F_\rho, A^E_\rho \in \mathbb{R}^{d\times d}$, $A^F_\rho = -\frac{1}{2}\widetilde{\mathcal{F}}^{\rm b}_{0,\rho}(0)$, and $A^E_\rho = -\frac{1}{2}\widetilde{\mathcal{E}}^{\rm b}_{,0\rho}(0)$. This crucially uses that fact that we apply the force approximation $\widetilde{\mathcal{F}}^{\rm b}_\ell$ at *every lattice site*, which makes it conservative. Note that Lemma B.1 and Theorem 3.1(i) imply

$$
|A^F_\rho - A^E_\rho| \le Ce^{-\eta(R_{\rm BUF}+|\rho|)},
$$

which together with (115) yields

$$
|Q_1| \le Ce^{-\eta R_{\rm BUF}}\|Dv\|^2_{\ell^2_\Upsilon}. \tag{116}
$$

Estimates for Q_2, Q_3. Lemma A.2 and $v \in \mathscr{W}^{\rm H}$ imply that

$$
\begin{aligned}
&\|v\|_{\ell^\infty} \le C\|Dv\|_{\ell^2_\Upsilon}\big(1 + \log R_{\rm MM}\big) \qquad \text{if } m = 2, \text{ and}\\
&\|v\|_{\ell^6} \le C\|Dv\|_{\ell^2_\Upsilon} \qquad \text{if } m = 3.
\end{aligned} \tag{117}
$$

Using (117), Lemma B.1, and Theorem 3.1(i), we have

$$
\begin{aligned}
|Q_2| &\le C\sum_{\ell\in\Lambda^{\rm QM}\setminus\Lambda^{\rm I}} e^{-\eta R_{\rm BUF}}|Dv(\ell)|_\Upsilon|v(\ell)|\\
&\le C\begin{cases} R_{\rm QM}\cdot\log R_{\rm MM}\cdot e^{-\eta R_{\rm BUF}}\|Dv\|^2_{\ell^2_\Upsilon} & \text{if } m = 2,\\ R_{\rm QM}\cdot e^{-\eta R_{\rm BUF}}\|Dv\|^2_{\ell^2_\Upsilon} & \text{if } m = 3\end{cases}\\
&\le CR_{\rm QM}\cdot\log R_{\rm MM}\cdot e^{-\eta R_{\rm BUF}}\|Dv\|^2_{\ell^2_\Upsilon}.
\end{aligned} \tag{118}
$$

Analogously, we have

$$|Q_3| \le CR_{\rm QM} \cdot \log R_{\rm MM} \cdot e^{-\eta R_{\rm BUF}} \|Dv\|^2_{\ell^2_\Upsilon}. \tag{119}$$

Estimate for Q_4. We can rewrite Q_4 as

$$\begin{aligned}
Q_4 &= \sum_{\ell\in\Lambda^{\rm I}} \big\langle \delta\mathcal{F}^{\rm H}_\ell(T^{\rm H}\bar u) - \delta\mathcal{F}^{\rm BUF}_\ell(T^{\rm H}\bar u), v\big\rangle v(\ell) + \sum_{\ell\in\Lambda^{\rm I}} \big\langle \delta\mathcal{F}^{\rm BUF}_\ell(T^{\rm H}\bar u) - \delta\widetilde{\mathcal{F}}^{\rm b}_\ell(u_0+T^{\rm H}\bar u), v\big\rangle v(\ell)\\
&- \sum_{\ell\in\Lambda^{\rm I}} \big\langle \delta\nabla_\ell\mathcal{E}^{\rm H}(T^{\rm H}\bar u) - \delta\nabla_\ell\mathcal{E}^{\rm BUF}(T^{\rm H}\bar u), v\big\rangle v(\ell)\\
&- \sum_{\ell\in\Lambda^{\rm I}} \big\langle \delta\nabla_\ell\mathcal{E}^{\rm BUF}(T^{\rm H}\bar u) - \delta\nabla_\ell\widetilde{\mathcal{E}}^{\rm b}(u_0+T^{\rm H}\bar u), v\big\rangle v(\ell)\\
&+ \sum_{\ell\in\Lambda^{\rm I}} \big\langle \delta\widetilde{\mathcal{F}}^{\rm b}_\ell(u_0+T^{\rm H}\bar u) - \delta\widetilde{\mathcal{F}}^{\rm b}_\ell(0), v\big\rangle v(\ell) - \sum_{\ell\in\Lambda^{\rm I}} \big\langle \delta\nabla_\ell\widetilde{\mathcal{E}}^{\rm b}(u_0+T^{\rm H}\bar u) - \delta\nabla_\ell\widetilde{\mathcal{E}}^{\rm b}(0), v\big\rangle v(\ell).
\end{aligned}$$

Using (68) and $\big|V^{B_{R_{\rm BUF}}(\ell)}_{\ell-\rho,\rho\xi\zeta} - V^{B_{R_{\rm BUF}}(\ell-\rho)}_{\ell-\rho,\rho\xi\zeta}\big| \le Ce^{-\eta\left(\left|R_{\rm BUF}-|\rho|\right|+|\rho|+|\xi|+|\zeta|\right)}$ (this is proved analogously to Lemma B.1), the last line can be bounded by

$$\begin{aligned}
&\Bigg| \sum_{\ell\in\Lambda^{\rm I}} \sum_{\rho\in\ell-\Lambda^{\rm I},\ |\rho|\le R_{\rm BUF}} \Big\langle \Big(\delta V^{B_{R_{\rm BUF}}(\ell)}_{\ell-\rho,\rho}\big(\mathsf{e}(\ell-\rho)+\mathsf{D}T^{\rm H}\bar u(\ell-\rho)\big) - \delta V^{B_{R_{\rm BUF}}(\ell)}_{\ell-\rho,\rho}(\mathbf{0})\Big)\\
&- \Big(\delta V^{B_{R_{\rm BUF}}(\ell-\rho)}_{\ell-\rho,\rho}\big(\mathsf{e}(\ell-\rho)+\mathsf{D}T^{\rm H}\bar u(\ell-\rho)\big) - \delta V^{B_{R_{\rm BUF}}(\ell-\rho)}_{\ell-\rho,\rho}(\mathbf{0})\Big), \mathsf{D}v(\ell-\rho)\Big\rangle\, v(\ell)\Bigg|\\
&= \Bigg| \sum_{\ell\in\Lambda^{\rm I}} \sum_{|\rho|\le R_{\rm BUF}} \int_0^1 \Big\langle \Big(\delta^2 V^{B_{R_{\rm BUF}}(\ell)}_{\ell-\rho,\rho}\big(t(\mathsf{e}(\ell-\rho)+\mathsf{D}T^{\rm H}\bar u(\ell-\rho))\big)\\
&- \delta^2 V^{B_{R_{\rm BUF}}(\ell-\rho)}_{\ell-\rho,\rho}\big(t(\mathsf{e}(\ell-\rho)+\mathsf{D}T^{\rm H}\bar u(\ell-\rho))\big)\Big)\big(\mathsf{e}(\ell-\rho)+\mathsf{D}T^{\rm H}\bar u(\ell-\rho)\big), \mathsf{D}v(\ell-\rho)\Big\rangle\, {\rm d}t\ v(\ell)\Bigg|\\
&\le C \sum_{\ell\in\Lambda^{\rm I'}} e^{-\eta R_{\rm BUF}} \cdot |\mathsf{e}(\ell)+\mathsf{D}T^{\rm H}\bar u(\ell)|_\Upsilon \cdot |\mathsf{D}v(\ell)|_\Upsilon \cdot \Big(\sum_{|\rho|\le R_{\rm BUF}} e^{-\eta|\rho|}\cdot|v(\ell+\rho)|\Big).
\end{aligned}$$

with $\Lambda^{\rm I'} := \{\ell\in\Lambda,\ \max\{0, R_{\rm QM}-2R_{\rm BUF}\} \le |\ell| \le R_{\rm QM}+2R_{\rm BUF}\}$. Using Theorem 3.6 and (117), we have

$$\begin{aligned}
|Q_4| &\le C \sum_{\ell\in\Lambda^{\rm I'}} \big(|\mathsf{e}(\ell)+\mathsf{D}T^{\rm H}\bar u(\ell)|^k_\Upsilon + e^{-\eta R_{\rm BUF}}\big)\cdot|\mathsf{D}v(\ell)|_\Upsilon \cdot \Big(\sum_{|\rho|\le R_{\rm BUF}} e^{-\eta|\rho|}\cdot|v(\ell+\rho)|\Big)\\
&\le CR^{1/2}_{\rm BUF}\cdot\|Dv\|^2_{\ell^2_\Upsilon} \begin{cases} \log R_{\rm MM}\big(R^{-2k+1/2}_{\rm QM}+e^{-\eta R_{\rm BUF}}\big) & \text{if } \mathbf{P} \text{ with } m=2,\\ R^{-3k+1/3}_{\rm QM}+e^{-\eta R_{\rm BUF}} & \text{if } \mathbf{P} \text{ with } m=3,\\ \log R_{\rm MM}\big(R^{-k+1/2}_{\rm QM}+e^{-\eta R_{\rm BUF}}\big) & \text{if } \mathbf{D}\end{cases}\\
&\le CR^{1/2}_{\rm BUF}\cdot\log R_{\rm MM}\cdot\big(R^{-k+1/2}_{\rm QM}+e^{-\eta R_{\rm BUF}}\big)\|Dv\|^2_{\ell^2_\Upsilon}. \qquad (120)
\end{aligned}$$

Estimate for Q_5. Let $\widetilde{\mathcal{F}}_\ell(v) := F_\ell(Px+v)$ and $\widetilde{\mathcal{E}}(v) := \sum_{\ell\in\Lambda}\big(E_\ell(Px_0+v) -$

$E_\ell(Px_0)\big)$; then $\widetilde{\mathcal{F}}_\ell(v) = \nabla_\ell \widetilde{\mathcal{E}}(v)$. Further, we define

$$\widehat{T}_k \widetilde{\mathcal{F}}_\ell(w) = \nabla_\ell \widehat{T}_{k+1} \widetilde{\mathcal{E}}(w) := \frac{\partial \widehat{T}_{k+1} \widetilde{\mathcal{E}}(w)}{\partial w_\ell}, \qquad \text{where} \tag{121}$$

$$\widehat{T}_{k+1} \widetilde{\mathcal{E}}(w) = T_{k+1} \widetilde{\mathcal{E}}(w) - \widetilde{\mathcal{E}}(0) - \big\langle \delta \widetilde{\mathcal{E}}(0), w \big\rangle.$$

Then, for any $\ell \in \Lambda^{\rm MM} \backslash \Lambda^{\rm I}$, we have

$$\begin{aligned}
&\Big| \Big\langle \big(\delta \mathcal{F}_\ell^{\rm H}(T^{\rm H}\bar{u}) - \delta \widetilde{\mathcal{F}}_\ell^{\rm b}(0)\big) - \big(\delta \nabla_\ell \mathcal{E}^{\rm H}(T^{\rm H}\bar{u}) - \delta \nabla_\ell \widetilde{\mathcal{E}}^{\rm b}(0)\big), v \Big\rangle \Big| \\
&\le \Big| \Big\langle \delta \mathcal{F}_\ell^{\rm H}(T^{\rm H}\bar{u}) - \delta \widetilde{\mathcal{F}}_\ell^{\rm b}(0) - \delta \widehat{T}_k \widetilde{\mathcal{F}}_\ell(u_0 + T^{\rm H}\bar{u}), v \Big\rangle \Big| \\
&\quad + \Big| \Big\langle \delta \nabla_\ell \mathcal{E}^{\rm H}(T^{\rm H}\bar{u}) - \delta \nabla_\ell \widetilde{\mathcal{E}}^{\rm b}(0) - \delta \nabla_\ell \widehat{T}_{k+1} \widetilde{\mathcal{E}}(u_0 + T^{\rm H}\bar{u}), v \Big\rangle \Big| \\
&\le C e^{-\eta R_{\rm BUF}} \sum_{|\rho| \le R_{\rm BUF}} e^{-\eta|\rho|} \cdot |\mathsf{D} v(\ell - \rho)|_\Upsilon \cdot \begin{cases} |\ell - \rho|^{-m} & \text{if } \mathbf{P}, \\ |\ell - \rho|^{-2} \log |\ell - \rho| & \text{if } \mathbf{D}. \end{cases}
\end{aligned}$$

Summing over $\ell \in \Lambda^{\rm MM} \setminus \Lambda^{\rm I}$ and applying (117), we obtain

$$|Q_5| \le C \, \log^2 \frac{R_{\rm MM}}{R_{\rm QM}} \cdot e^{-\eta R_{\rm BUF}} \|Dv\|_{\ell^2_\Upsilon}^2. \tag{122}$$

(For case **P** one obtains $\log \frac{R_{\rm MM}}{R_{\rm QM}}$ instead of $\log^2 \frac{R_{\rm MM}}{R_{\rm QM}}$, but this is qualitatively the same as replacing the unknown exponent η with $\eta/2$; hence we ignore this small improvement.)

Combining (114), (116), (118), (119), (120), and (122), we finally deduce that

$$\big| \big\langle \big(\delta \mathcal{F}^{\rm H}(T^{\rm H}\bar{u}) - \delta^2 \mathcal{E}^{\rm H}(T^{\rm H}\bar{u})\big) v, v \big\rangle \big| \le C \left(R_{\rm QM}^{-k+3/4} + e^{-\frac{\eta}{4} R_{\rm BUF}} \right) \|Dv\|_{\ell^2_\Upsilon}^2$$

provided that $R_{\rm QM} > \log^4 R_{\rm MM}$, $R_{\rm BUF} > \frac{3}{\eta} \log R_{\rm QM}$, $R_{\rm BUF} > \frac{3}{\eta} \log\log R_{\rm MM}$. This completes the proof. ∎

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